VOLUME 19
NUMBER 4

JOURNAL OF

APRIL
1942

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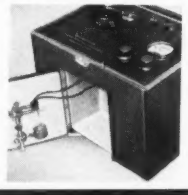

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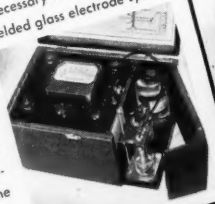

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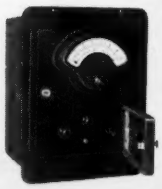

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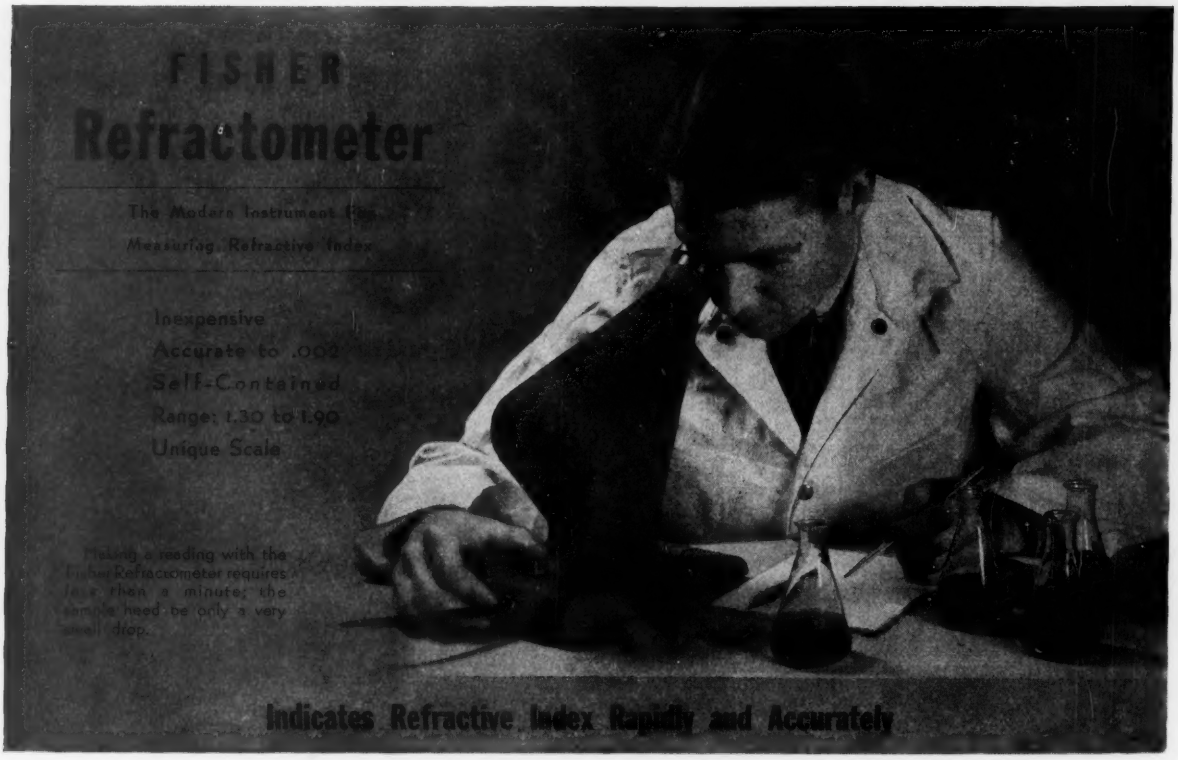
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Inexpensive
Accurate to .002
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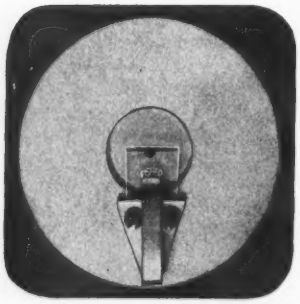
Range: 1.30 to 1.90
Unique Scale
Making a reading with the Fisher Refractometer requires less than a minute; the sample need be only a very small drop.
Indicates Refractive Index Rapidly and Accurately

The Fisher Refractometer is an inexpensive instrument which measures the refractive index of liquids with an accuracy of ±.002 units. Its operation is so simple and its cost so low in comparison with that of other refractometers that its advantages can now be fully realized by educational laboratories.



The sample placed in the wedge-shape well at the eyepiece refracts light seen through the aperture.

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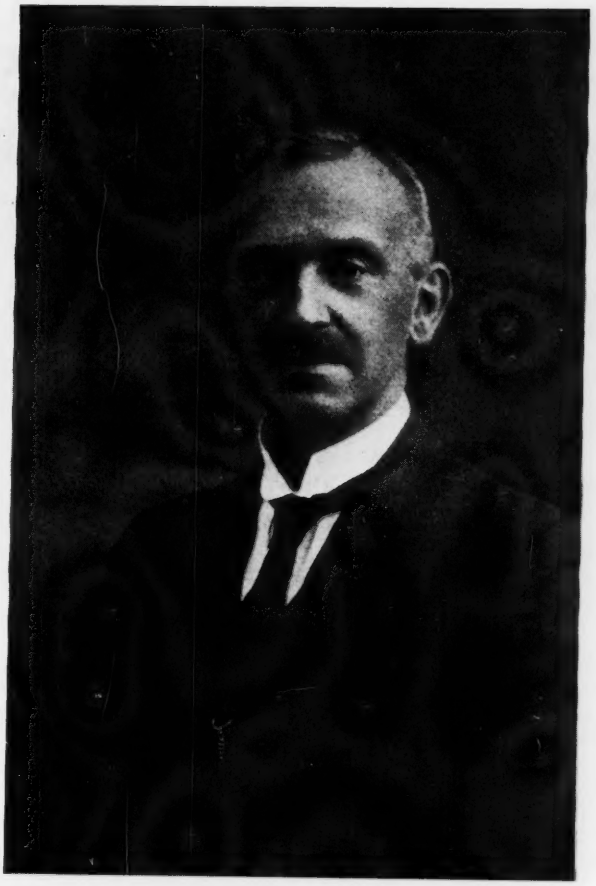

Hugo Rudolph Kruyt
(1882–)

Contributed by H. S. van Klooster, Rensselaer Polytechnic Institute

(For biographical sketch of Hugo Rudolph Kruyt, see page 165.)

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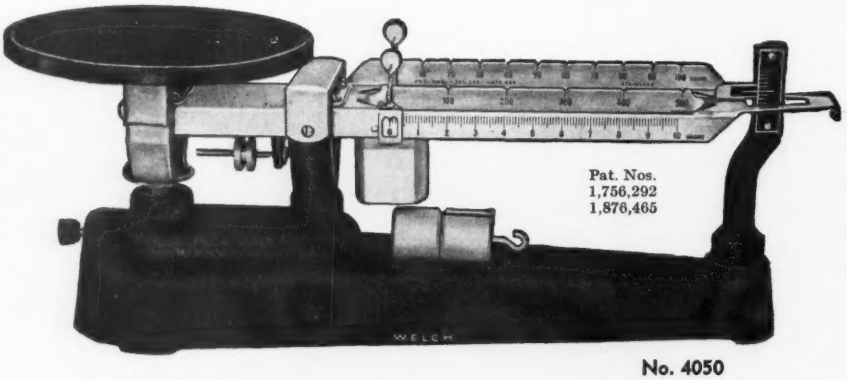

No. 4050

Capacity:
1610 grams
Sensitivity:
0.1 g.

The first triple-beam trip scale was developed by Welch and this newest design contains many noteworthy and valuable improvements.

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Every tiny screw, rivet and nut in this balance is of stainless steel. Laboratory fumes have practically no effect on the stainless steel parts, which were tested in strong chemical solutions for a month's period and showed negligible penetration, with virtually complete corrosion resistance. This insures bright, clear, easily read scales for many years—an exclusive Welch advantage. The use of stainless steel makes possible fine, sharp, easily read graduations on the beams.

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The knife-edges are hard, corrosion-resistant Cobalite, a cobalt-chromium-tungsten alloy, used so satisfactorily in industrial applications. Heretofore these were found only in "extra-cost," high-grade analytical balances. Cobalite is used on high-speed cutting tools, automobile exhaust valves, and in almost every place where hard, smooth, corrosion-resistant edges are needed. It provides a life 10 to 20 times that of hardened steel. The bearings for these knife edges are selected quality agate bearings.

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In the Welch triple-beam trip scale, the extra weights are provided, and the die-cast base is molded with a semi-circular depression for holding the extra weight. One weight and hanger only provides a capacity of 1110 g. and by the addition of an extra weight the total capacity is brought to 1610 grams.

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The stainless steel cover is provided so that no materials can fall into the agate bearings which support the Cobalite knife-edges. This feature will be particularly appreciated in the chemistry laboratory where so often balances of this type are ruined, and particularly those with ferrous knife-edges or bearings, by some of the salts falling on the knife-edges and into the bearings.

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Editor's Outlook

IN HIS attitude toward present-day "Wonders of Science" the intelligently informed person is neither overcredulous nor ultrasceptical. While familiar with the spectacular successes of modern science and technology he is also aware of their limitations. He does not expect the problem of perpetual motion to be solved "any day now." On the other hand, with the clear facts of artificial transmutation before him, he is not upset by the apparent prospect of atomic power from uranium fission. Sound scientific realism is one of the objectives of science education, and we are making some progress toward it.

We must face the present course of world events with our customary, realistic habit of mind and training. The outlook is not a bright one, at the moment of writing this, with the western Pacific area almost completely overrun by the enemy. This can hardly be regarded with complacency, but let us neither minimize the peril nor underestimate our capacity to meet it. We recently came across the following, in an editorial entitled "1942 Comes to America" in *Food Materials and Equipment*, which fits the situation completely:

> "We have inherited power. But we have also inherited a tradition; a tradition of courage in the face of obstacles which often seemed insuperable; a tradition of accomplishing the impossible; a tradition of stubbornly refusing to believe that 'it can't be done,' of looking constantly for new methods, new knowledge, which makes it possible for us to say triumphantly, 'it *can* be done—we've done it!'"

Collectively, we have been accused of being apathetic about the war. But a peace-loving nation as large as ours cannot go on the warpath overnight. And we have already made considerable progress. In the beginning one frequently heard the remark: "The normal course of life and business shouldn't be interfered with any more than *necessary*." We don't hear this very often any more, fortunately; it is a sentiment which could defeat us. It is equivalent to saying that we should proceed with this war as slowly as possible. On the contrary, we should be ready—even anxious—to disrupt our normal lives entirely, in order to get on with this business and get it over with.

Which brings us to the point. We have been receiving requests for enlightenment on the specific opportunities and duties of chemistry teachers at the present time. "What can we do that will be of real and immediate help?" The educational literature is filling up with general answers to this question, applying to all kinds of teachers. There is a feeling, however, that the science teacher has a rather particular problem.

The burden can, of course, be put upon the individual to decide what contribution his particular training and ability best fit him to make, but something more specific is needed. This we will hope to supply, from time to time, as suggestions come in to us. We are making a start in this direction in the article by A. M. Patterson this month.

The science teacher should regard himself as particularly qualified to face the problems of this war, and by his attitude toward them should set an example to others. If teachers, scientists, and engineers cannot see their way clearly in a war which is so largely technological there is little hope for others to do so.

It has become clearly evident that one of our biggest and most important problems is the survey and allocation of our available manpower. Where do we need to apply human efforts most urgently; how many men do we have who are able to do these things; how can we distribute these men most efficiently, so that each will be given a chance to do what he is best *able* to do? These are the most pressing questions. In order to stop the competition between various agencies and services for the limited number of available men it would seem necessary to put the problem in the hands of a centralized agency of some sort, with power to make and enforce decisions. Meanwhile, and in addition to this administrative expedient, much can doubtless be done in a more decentralized manner to help solve the difficulty.

There is something fundamental here. We are struggling to uphold the democratic ideal in an unsympathetic world. It is scarcely fitting that we should despair of a democratic solution of our own problems. A clear, public presentation of a difficulty; a period of thought, discussion, and enlightenment; followed by a crystallization of public opinion and determination—this has been the democratic method. Perhaps it will avail us in the present emergency, if time isn't too short. There has been too much sitting back and waiting until "the Government tells us what to do." We need leadership, yes, badly. But let us not permit our wishful desire for it to blind us to our own responsibility in the solution of these problems. Our various organized groups, especially the educational agencies, by means of intelligent discussion and advice, can lay the groundwork of an enlightened public opinion upon which, in the long run, any solution must be based.

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What's Been Going On

THERE are about 200 uses for rubber in the modern automobile.

Our consumption of rubber in 1917 was only about 60,000 tons a year, but in 1941 it was nearly that much a month.

More than 2000 Hevea trees, raised in Miami during the last 17 years, are producing latex that compares favorably with that obtained from the East Indies.

Twenty-nine varieties of synthetic rubber have been studied critically. Among the more satisfactory products may be listed Ameripol, Buna S, Butyl rubber, Chemigum, Hycar, Koroseal, Methyl rubber, Neoprene, Perbunan, Sovprene, Synthal, Thiokol, and Vistanex.

When vats of milkweed are inoculated with certain forms of bacteria and allowed to ferment, a rubber-like product is obtained which is particularly adapted to bullet-proofing gasoline tanks, according to W. A. Sharp, a California inventor.

The guayule plant, which has been developed in the arid regions of the Southwest by General Tire and Rubber Company, has a rubber content of about 23 per cent. It is believed that selection would increase this figure to about 30 per cent. Under a five-year cycle plan, it is believed that this plant will produce rubber for about twenty cents per pound.

A dandelion known as kok-sagnyz, discovered and grown in Russia, has merit as a rubber-producing crop that appears to be equal or superior to that of the guayule plant that is being developed in the Southwest.

The medium sized military tank, which is the popular size in America, weighs 30 tons, and its construction requires as much steel as 500 refrigerators and as much rubber as 87 average auto tires.

One of the newer patented uses for nylon is as a bearing for machinery. It requires neither oil nor water lubrication.

The use of nylon for insulation permits the manufacture of motors that require about 10 to 15 per cent less space.

The by-products of the citrus fruit industry, pectin, citric acid, and orange and lemon oil, amount to about $2,500,000 annually.

The electric refrigerators of 1942, if any, will have more than fifty plastic parts.

Dr. Brown of the University of California reports that vitamin deficiency for just one day may result in night blindness that will materially increase one's accident hazard in night driving.

The grease reclamation plant in Washington, D. C., took advantage of the rise in prices and disposed of grease reclaimed from garbage to the amount of $65,000.

"What would you say if some chemical engineer said he could drill a hole through a piece of hard steel with a tiny jet of salt water? So would I! But Dr. Burgess did just that at the Chicago meeting of the Electrochemical Society. By setting up an electrical circuit through a salt bridge and the metal the hardest metals may be drilled. Tungsten carbide may also be cut in this manner."

Dr. E. Berl, of Carnegie Institute of Technology, has converted vegetable carbohydrate into a synthetic bitumen, then into an asphalt and crude oil, and finally into kerosene, gasoline, and other petroleum products.

Studies by DeBakey and Giles of Tulane University indicate that an acetone solution of vinyl resins, when painted onto the skin before making the incision, aids in keeping germs out of a surgical wound.

The most efficient engine, presumably, is a combination mercury-vapor engine and a steam engine at Kearny, New Jersey, which develops 51,000 kilowatts of electricity at the rate of one kilowatt-hour for every half pound of fuel oil consumed.

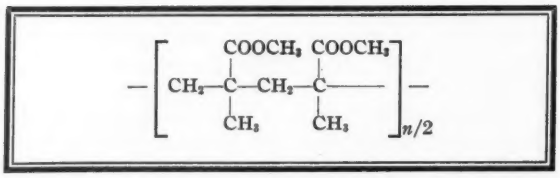
Thiourea is put up in tablet form and sold as Frulite to prevent discoloration of sliced or cut fruits.

Synthetic glycerol may now be produced by (*a*) high temperature chlorination of propane to give allyl chloride, which is then treated with hypochlorous acid and subsequent hydrolysis, (*b*) by the fermentation of carbohydrates, (*c*) by the hydrogenolysis of carbohydrates, or (*d*) from refinery gases by the Battelle catalytic process.

Soon after the first of May, the production capacity for aluminum will be increased about 150,000,000 pounds annually as the result of new plants that were started in January of this year. These plants are being financed by the DPC, but will be operated by the Aluminum Company of America.

—Ed. F. Degering

FORMULA OF THE MONTH



Poly-methyl methacrylate

The polymer of *n* molecules of methyl methacrylate, which composes synthetic resins of the type of Lucite and Plexiglas.

Some Personal Recollections of Alfred Werner

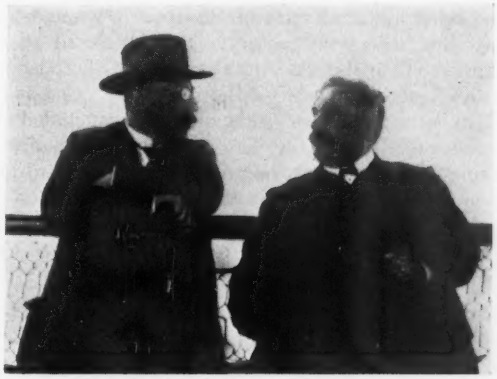
E. BERL

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

ALFRED WERNER was born in 1866 in Mulhouse in Alsace. His father was a man of very small means. Young Werner wanted to study chemistry at the Technical University of Zurich which was one of the great teaching institutions in Europe. But he was not very strong in mathematics and only by a happy accident did he overcome difficulties in this line before he was accepted as a student at the old Zurich Polytechnicum, where he studied under Hantzsch and Lunge.

In 1886–88 Arrhenius and van't Hoff founded what we now call classical physical chemistry. The theory of electrolytic dissociation was the great contribution of these two. In 1875 van't Hoff had already published "La chimie dans l'espace" at the same time that Le Bel developed similar viewpoints. With this publication he launched the stereochemistry which in 1867 had been suggested by his teacher, August Kekulé. In 1889 when Hantzsch was Werner's professor in organic chemistry, the 23-year-old student, influenced by the views of van't Hoff, Le Bel, and Arrhenius, suggested to him that nitrogen compounds must exist in different stereochemical modifications just like carbon compounds. The three valence forces of nitrogen, argued Werner, are oriented toward three corners of a tetrahedron, in the fourth corner of which is the nitrogen atom. Hantzsch did not accept this viewpoint at first, but the next day he came to Werner and told him he believed he was right. As a consequence, in 1890 the first paper on stereo-oximes was published. Werner became assistant to Lunge, who, soon afterward, said to him, "My dear Werner, you are fired as my assistant. You are too good for this position. I will use my influence to convince your father to let you continue your studies elsewhere and devote yourself to teaching and research." Werner spent one year in Paris with Marcelin Berthelot. I am convinced that the money for this was provided by Lunge. Werner returned to Zurich, soon to become associate professor. He gave a course on the theory of inorganic compounds. One night, after working on his lectures, he dreamed his coordination theory, just as Kekulé in 1858 and in 1865 had dreamed of structural chemistry and the benzene ring. Exactly like Kekulé, Werner's brain had subconsciously worked out what is now known as the coordination theory of complex compounds.

Werner is the representative of the "romantic type" of great men who perform their best deeds in their younger years. His coördination theory was developed in 1893 and explains the composition of compounds of first and higher order, the so-called "molecular compounds." It was afterward applied with success to organic problems, and is the most important enlargement of Kekulé's doctrine of valence. In 1893 Werner also predicted that optical isomers of inorganic molecular compounds must exist, a prediction later verified by many examples. Among the latter were some of the cobalt salts, prepared in 1911 by the collaboration of V. L. King, now technical director of the Calco Chemical Company.



PAUL PFEIFFER AND ALFRED WERNER

I wrote my dissertation under Werner and afterward became his scientific assistant. In his private laboratory he had a small table reserved for himself. Many small glass bowls, a microburner, and two platinum spatulas were his tools. A large cabinet was filled with hundreds of preparations, without any visible system of arrangement. He became very angry when I tried to bring order into this multitude of bottles and glasses, and claimed he could no longer find the preparations he wanted. He could not stand the odor of nitrobenzene. When I wanted to be alone I had simply to heat some nitrobenzene. When he opened the door which connected the laboratory with his tiny office and smelled the odor of nitrobenzene, he closed the door and was not seen for hours.

He did not believe in separate institutions for research and teaching, but told me several times that research and teaching form a happy symbiosis. Teaching forces the research man to become acquainted with facts and theories outside his own special field which may happily influence his research work which, on the other hand, gives the teacher a better insight in those matters which he has to teach to his pupils.

I was in Zurich from 1899 to 1910. Zurich, called the Limmat-Athenes, was the rendezvous of many great scientists. The meetings in the Zurich Chemical Society with Werner, Pfeiffer, Grün, Lunge, Eugene Bamberger, and from 1906 on with Willstätter, were a delight for us younger scientists. One day an associate

professor gave a talk. Werner believed that more experiments should be carried out in order to establish a theoretical conclusion. The young professor said: "I have already sent the manuscript to the *Berichte*. I cannot do any further work for another five or six months." Werner became extremely angry. "You do it, and it makes no difference if you have to work another 50 or 60 years," he said.

In the fall of 1913 when I was the chief chemist of the nitro rayon factory in Tubize, Werner wrote me that he would be in Brussels on the occasion of the meeting of the scientific academies of Europe. I wanted him to see the big rayon factory. It was closed to all strangers, but in this case the chairman of the board, a French count, made an exception, and Werner was invited to come to Tubize. The operations included the nitration of cellulose, the dissolution of collodion, the spinning and twisting operations, the denitration, bleaching, etc. Werner did not show any interest at all. Finally, I showed him the recovery of ether-alcohol vapors from the spinning rooms. I explained that ether with strong sulfuric acid forms a molecular compound with a very small ether vapor pressure and that it can be decomposed rather easily by dilution with water and by steaming. When he heard the word "molecular compound," he became deeply interested and the rest of the day, and the following sleepless night, he came back again and again to the statement: "Now I see how little we know. We tell our students that if ether is taken up by strong sulfuric acid, ethyl sulfuric acid is formed. Now you tell me this is wrong and that a rather labile oxonium compound is the product of reaction."

I saw Werner last in May, 1914, when the Swiss Chemical Society honored him as the winner of the 1913 Nobel prize. We had a meeting in Solothurn. From there I went to Zurich and attended one of his classes. He and I were deeply touched and this was the last time that I saw him. In 1915 he became seriously ill. He had to give up his academic activity, which was taken over by Paul Pfeiffer and Paul Karrer, and died from arteriosclerosis in 1919.

Acids and Bases in Organic Chemistry

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DEFINITIONS

MOST organic acids fall into the class of "hydrogen acids." These are defined by the Brønsted equation[1]

$$\text{Acid} \rightleftharpoons \text{Base} + H^+$$

The acid and base which are connected by this expression in a given case form an acid-base system. The base corresponding to a given acid is known as its conjugate base and vice versa. For example, acetic acid and its conjugate base, acetate ion, constitute an acid-base system. Methyl amine and its conjugate acid, methylammonium ion, form another type of acid-base system.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$$

These equations represent *potential* ionizations, the extent of which may be measured only relatively. That is, one may treat the acid of one acid-base system with the base of another and from the equilibrium constant of the reaction

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

determine the relative strengths of the two acid-base systems. Thus, the relative strengths of the two acid-base systems mentioned above may be obtained by mixing acetic acid and methyl amine, or acetate ion and methylammonium ion, in some suitable medium such as water or methanol and observing the position of equilibrium in the reversible reaction

$$CH_3COOH + CH_3NH_2 \rightleftharpoons CH_3NH_3^+ + CH_3COO^-$$

This procedure is not unique since the same practice is employed with the analogous oxidation-reduction systems which are defined by the equation

$$\text{Reductant} \rightleftharpoons \text{Oxidant} + \epsilon^-$$

and which are measured relatively by determining equilibria for reactions of the type

$$\text{Red}_1 + \text{Ox}_2 \rightleftharpoons \text{Red}_2 + \text{Ox}_1$$

CHARGE TYPES OF ACID-BASE SYSTEMS

The examples of acid-base systems given above illustrate the two commonly occurring charge types: (1) those like sulfonic acids, carboxylic acids, and phenols which consist of an uncharged acid, HA, with its conjugate anionic base, A^-; and (2) those like the alkylammonium and hydronium (oxonium) ions which consist of a cationic acid, BH^+, with its uncharged base, B.

ACIDITY CONSTANTS

Unless otherwise stated the acidity constants of acid-base systems refer to their interaction with the water system

[1] BRØNSTED, *Chem. Rev.*, 5, 231 (1928).

$$H_3O^+ \rightleftharpoons H_2O + H^+$$

water, itself, forming the medium. Under these circumstances the reaction involved in the case of an uncharged acid, HA, may be represented by the equation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

for which the equilibrium constant, K, is given by

$$K = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

Since the concentration of water is practically constant in dilute solutions, $[H_2O]$ may be combined with K in the constant, K_a, which is the *acidity constant.* This is identical with the classical ionization constant for acids.

$$K_a = K[H_2O] = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Since K_a involves concentrations, it is known as the "concentration" constant. In a given solvent, its value depends on the ionic strength. Extrapolation of K_a values to zero ionic strength yields K_a', which is the so-called "thermodynamic" acidity constant.

In logarithmic notation, the previous equation becomes

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

When the conjugate acid and base concentrations are equal,

$$pK_a = pH$$

This leads to a convenient method of determining acidity constants by measuring the pH of a solution of an acid, half of which has been converted to its conjugate base by means of a strong base such as hydroxyl ion.

In the case of a cationic acid, BH^+, the equilibrium involved in water solution is

$$BH^+ + H_2O \rightleftharpoons H_3O^+ + B$$

Hence

$$K = \frac{[H_3O^+]\,[B]}{[BH^+]\,[H_2O]}$$

$$K_a = K\,[H_2O] = \frac{[H_3O^+]\,[B]}{[BH^+]}$$

$$pK_a = pH - \log \frac{[B]}{[BH^+]}$$

Although pK_a's relate to their respective acid-base systems, they are referred to as "acidity constants" or simply as "acid strengths." The smaller the pK_a value, the greater is the strength of the acid, that is, the greater is the tendency of the acid to be converted to its conjugate base by the loss of a proton, and conversely, the weaker is the tendency for the base to accept a proton and be converted to the conjugate acid. For convenience in discussion, acid strengths may be classified as shown in Table 1. The symbols indicated in the table will be found useful.

TABLE 1

CLASSIFICATION OF ACID-BASE STRENGTHS

pK_a	Conjugate Acid	Conjugate Base	Examples
<2	Strong (A_s)	Neutral (N)	RSO_3H:RSO_3^- CCl_3COOH:CCl_3COO^- Picric Acid:Picrate Ion$^-$ $Ar_2NH_2^+$:Ar_2NH
2–7	Intermediate (A_i)	Weak (B_w)	CH_3COOH:CH_3COO^- 2,4-Dinitrophenol:2,4-Dinitrophenolate Ion$^-$ $ArNH_3^+$:$ArNH_2$
8–12	Weak (A_w)	Intermediate (B_i)	$ArOH$:ArO^- RCH_2NO_2:$RCHNO_2^-$ RNH_3^+:RNH_2
>12	Neutral (N)	Strong (B_s)	ROH:RO^- Guanidinium Ion$^+$:Guanidine

The classical ionization constant, K_i, for bases of the amine type is obtained from the equation

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K = \frac{[BH^+]\,[OH^-]}{[B]\,[H_2O]}$$

$$K_i = K\,[H_2O] = \frac{[BH^+]\,[OH^-]}{[B]}$$

K_i may be related to K_a for the system, BH^+:B, by combining it with K_w, the ion product or autoprotolysis constant of water. The latter is derived by considering water to function both as an acid and as a base.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K = \frac{[H_3O^+]\,[OH^-]}{[H_2O]^2}$$

Since, in dilute solution, $[H_2O]$ is constant,

$$K_w = K\,[H_2O]^2 = [H_3O^+]\,[OH^-]$$

At 25°C. $K_w = 10^{-14}$ or $pK_w = 14$.
Dividing K_w by K_i,

$$\frac{K_w}{K_i} = \frac{[H_3O^+]\,\cancel{[OH^-]}\,[B]}{[BH^+]\,\cancel{[OH^-]}} = K_a$$

Hence, $pK_a = 14 - pK_i$.

ACIDITY CONSTANTS IN METHANOL

If an uncharged acid, HA, such as a carboxylic acid or a phenol is dissolved in methanol, the following equilibrium is established.

$$HA + CH_3OH \rightleftharpoons CH_3OH_2^+ + A^-$$

$$K = \frac{[CH_3OH_2^+]\,[A^-]}{[HA]\,[CH_3OH]}$$

$$K_{a(MeOH)} = K\,[CH_3OH] = \frac{[CH_3OH_2^+]\,[A^-]}{[HA]}$$

$$pK_{a(MeOH)} = pH_{(MeOH)} - \log \frac{[A^-]}{[HA]}$$

In practice, the values of $pK_{a(MeOH)}$ are found to be about five units larger than $pK_{a(H_2O)}$. This decreased acidity in methanol is to be attributed mainly to the lower dielectric constant of methanol, which hinders the formation of ions. Note that an acid-base reaction between an uncharged acid and an uncharged base results in the production of two ions from two uncharged molecules. In the case of cationic acids, BH^+, however, the effect of dielectric constant is not great since

the acid-base reaction with an uncharged base involves no change in the number of ions present. The pK_a's of the anilinium:aniline and the ammonium:ammonia systems are 1.4 units higher in methanol than in water.[2]

THE INFLUENCE OF IONIC STRENGTH

Acid-base systems are more or less sensitive to variations in the ionic strength depending on the charge type involved. Cationic acid systems are affected only little by changes in ionic strength while uncharged acid systems show an increase in acidity with increasing ionic strength. This shift may be predicted quantitatively by means of the Debye-Hückel theory, and, in methanol, amounts to about one unit of pK_a between the ionic strengths 0.00 and 0.25.[2]

FEEBLE ACIDS AND BASES

Although from a practical point of view the term *acid* is usually limited to substances belonging to acid-base systems of pK_a less than about 12 to 13 and the term *base* to substances belonging to systems of pK_a greater than about 1 to 2, this limitation is arbitrary. Actually, by choosing suitable solvents, the range of detectable acids and bases may be greatly extended. Thus, by operating in glacial acetic acid, conjugate bases have been studied whose pK_a's ranged down to -1.6.[3] In concentrated sulfuric acid, this region has been extended still further down to -9.3 (trinitroanilinium: trinitroaniline).[4] On the other hand, by utilizing liquid ammonia or ether solutions, acids as feeble as triphenylmethane ($pK_a=33$) have been studied.[5] For the present purpose, however, it will be convenient to consider as "neutral," conjugate bases of systems of pK_a less than 2 and conjugate acids of systems of pK_a greater than 12. (See Table 1.)

AMPHOLYTES

Species which function both as conjugate acids and as conjugate bases are known as *ampholytes*. Common examples are the amino acids and the aminophenols. Glycine, for instance, participates in two equilibria:

$$^{+}NH_3CH_2COOH \rightleftharpoons {}^{+}NH_3CH_2COO^- + H^+ \quad (pK_a = 2.3)$$
$$^{+}NH_3CH_2COO^- \rightleftharpoons NH_2CH_2COO^- + H^+ \quad (pK_a = 9.7)$$

In other words, $^{+}NH_3CH_2COOH$ is a dibasic acid with ionizations corresponding to pK_a's 2.3 and 9.7. In general the product of the primary ionization of a dibasic acid satisfies the definition of an ampholyte. Ampholytes may be of various charge types: (1) *uncharged* (or dipolar ions), such as glycine; (2) *cationic*, such as $NH_2CH_2CH_2NH_3^+$; and (3) *anionic*, such as $HOCOCH_2CH_2COO^-$.

It is convenient to apply here, too, the limitations on acid strengths discussed in the previous section. Without this restriction, many substances commonly regarded simply as acids *or* bases must be classified as ampholytes. Thus, benzoic acid, which in water functions as an acid in the system, $C_6H_5COOH:C_6H_5COO^-$ ($pK_a = 4.2$), may, in concentrated sulfuric acid, also function as a base in the system, $C_6H_5COOH_2^+:C_6H_5COOH$ ($pK_a = -7.3$).[6] Aniline, which in water functions as a base in the system, $C_6H_5NH_3^+:C_6H_5NH_2$ ($pK_a = 4.6$), may in ether solution also function as an acid in the system, $C_6H_5NH_2:C_6H_5NH^-$ ($pK_a = 27$).[5]

STRUCTURAL TYPES OF ACIDS AND BASES

Water, as has been seen, possesses feeble acidic and basic properties which depend upon its ability to enter into two equilibria.

$$H_3O^+ \rightleftharpoons H_2O + H^+ \quad \text{(as a base)}$$
$$H_2O \rightleftharpoons OH^- + H^+ \quad \text{(as an acid)}$$

Similar behavior is shown by anhydrous ammonia.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad \text{(as a base)}$$
$$NH_3 \rightleftharpoons NH_2^- + H^+ \quad \text{(as an acid)}$$

Many organic compounds may now be looked upon as substitution products of water or ammonia. Phenol, for instance, may be considered phenylated water, aniline as phenylated ammonia. It is of interest that the influence which the phenyl group has on the acidity or basicity of water is paralleled by its influence on ammonia. Thus, just as phenol is a stronger acid than water, and phenylhydronium ion than hydronium ion (that is, phenol is a weaker base than water), so also is aniline a stronger acid than ammonia and anilinium ion a stronger acid than ammonium ion (that is, aniline is a weaker base than ammonia). These facts indicate that the introduction of the phenyl group into a hydrogen compound generally has an acidifying effect. By pursuing this treatment, practically all the hydrogen acids of organic chemistry may be related to four fundamental structures (hydrogen, water, ammonia, and methane) and to some twelve substituent groups [Cl, NO, NO_2, RSO, RSO_2, CN, RCO, RC≡C, RCH=CH, C_6H_5, R_3N^+, and R (aliphatic)]. Of these groups all but the last have an acidifying effect. Only the alkyl groups typified by methyl have a basifying influence. When sulfur replaces oxygen, either in the parent substance or in the substituent, an increase in acidity is observed (compare H_2S with H_2O).

A few examples of this scheme may now be in order. Consider the influence of the nitro group on the acidity of hydrogen, water, ammonia, and methane. Replacement of one hydrogen atom in the neutral hydrogen molecule by the nitro group yields nitrous acid, a weak acid; in the neutral water molecule, yields nitric acid, a strong acid; in the intermediate base, ammonia, yields the intermediate acid, nitramide; in the neutral methane, yields nitromethane, a weak acid. Further replacements of hydrogen atoms continue to

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[2] KOLTHOFF AND GUSS, *J. Am. Chem. Soc.*, **61**, 330 (1939).
[3] HALL AND MEYER, *J. Am. Chem. Soc.*, **62**, 2493 (1940).
[4] (*a*) HAMMETT AND DEYRUP, *J. Am. Chem. Soc.*, **54**, 2721 (1932); (*b*) HAMMETT AND PAUL, *ibid.*, **56**, 827 (1934).
[5] (*a*) CONANT AND WHELAND, *J. Am. Chem. Soc.*, **54**, 1212 (1932); (*b*) MCEWEN, *ibid.*, **58**, 1124 (1936).
[6] FLEXSER AND HAMMETT, *J. Am. Chem. Soc.*, **60**, 885 (1938).

TABLE 2

STRUCTURAL TYPES OF ACID-BASE SYSTEMS

Groups	*Types* H_2	H_2O	NH_3	CH_4
Cl	HCl (A_s)	HOCl (A_w)	NH_2Cl (N)	CH_3Cl (N) CH_2Cl_2 (N) $CHCl_3$ (N)*
NO	HNO (A_w)	HONO (A_i)	NH_2NO (N)†	$CH_2NO \rightarrow$ $CH_2{=}NOH$ (A_w)
NO_2	HNO_2 (A_i)	$HONO_2$ (A_s)	NH_2NO_2 (A_i)	CH_3NO_2 (A_w) $CH_2(NO_2)_2$ (A_i) $CH(NO_2)_3$ (A_s)
RSO RSO_2	RSOH (A_w) RSO_2H (A_s)	RSOOH (A_s) RSO_2OH (A_s)	$RSONH_2$ (?) RSO_2NH_2 (A_w) $(RSO_2)_2NH$ (A_s)	$RSOCH_3$ (N) RSO_2CH_3 (N) $(RSO_2)_2CH_2$ (A_w) $(RSO_2)_3CH$ (?)
CN	HCN (A_w)	HOCN (A_i)	NH_2CN (A_w) $NH(CN)_2$ (A_i)*	CH_3CN (N) $CH_2(CN)_2$ (A_w) $CH(CN)_3$ (A_s)
RCO ROCO	RCHO (N)	RCOOH (A_i)	$RCONH_2$ (N) $(RCO)_2NH$ (A_w) $(RCO)_3N$ (A_i)	$RCOCH_3$ (N) $(RCO)_2CH_2$ (A_w) $(RCO)_3CH$ (A_i)
$RC{\equiv}C$	$RC{\equiv}CH$ (N)*	$RC{\equiv}COH \rightarrow$ $RCH{=}C{=}O$ (A_i)	$RC{\equiv}CNH_2 \rightarrow$ $RCH{=}C{=}NH \rightarrow$ RCH_2CN (N)	$RC{\equiv}CCH_3$ (N) $(RC{\equiv}C)_2CH_2$ (N) $(RC{\equiv}C)_3CH$ (?)
$RCH{=}CH$	$RCH{=}CH_2$ (N)	$RCH{=}CHOH$ (A_w)	$RCH{=}CHNH_2$ (B_w) $(RCH{=}CH)_2NH$ (N)	$RCH{=}CHCH_3$ (N) $(RCH{=}CH)_2CH_2$ (N) $(RCH{=}CH)_3CH$ (N)
C_6H_5	C_6H_6 (N)	C_6H_5OH (A_w)	$C_6H_5NH_2$ (B_w) $(C_6H_5)_2NH$ (N) $(C_6H_5)_3N$ (N)	$C_6H_5CH_3$ (N) $(C_6H_5)_2CH_2$ (N) $(C_6H_5)_3CH$ (N)
R_3N^+	R_3NH^+ (A_w)	R_3NOH^+ (A_i)	$R_3NNH_2^+$ (B_w)	$R_3NCH_3^+$ (N) $(R_3N)_2CH_2^{++}$ (N) $(R_3N)_3CH^{+++}$ (?)
R	RH (N)	ROH (N)	RNH_2 (B_i) R_2NH (B_i) R_3N (B_i)	RCH_3 (N) R_2CH_2 (N) R_3CH (N)

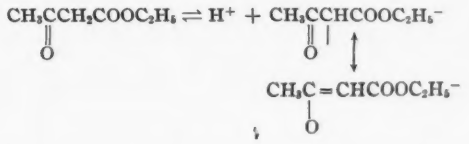
* Potential acidity indicated by aldol condensation with acetone and by hydrogen bond formation.
† Estimated from derivatives.

increase the acidity. Thus, dinitromethane is an intermediate acid, and trinitromethane (nitroform) a strong acid. The cyano group when introduced into hydrogen yields hydrogen cyanide, a weak acid; into water, cyanic acid, an intermediate acid; into ammonia, cyanamide, a weak acid; and into methane, acetonitrile, which is still neutral although dicyanomethane (malonitrile) is a weak acid, and tricyanomethane (cyanoform) a strong acid. The RCO group introduced into hydrogen yields RCHO, still a neutral substance; into water, RCOOH, an intermediate acid; into ammonia, the neutral $RCONH_2$ and the weakly acidic $(RCO)_2NH$; and into methane, $RCOCH_3$, which is neutral, $(RCO)_2CH_2$, a weak acid, and $(RCO)_3CH$, an intermediate acid.

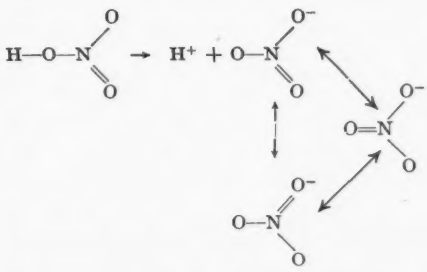
The only established basifying group, the alkyl groups typified by methyl, are relatively weak in effect. Furthermore, they are defective in their additive character as may be judged by comparing the strengths of the corresponding primary, secondary, and tertiary amines. The average change in pK_a for the introduction of the first alkyl group into ammonia is +1.32, for the second, +0.34, and for the third, −0.66.[7]

THE INFLUENCE OF RESONANCE

The ability of acidifying groups to enhance the release of protons has been ascribed to their tendency to attract the electrons of the covalence binding the proton. Since resonance stabilizes a substance this tendency is heightened when the ion which results from the discharge of a proton forms a resonating system or resonance hybrid. This is particularly true if symmetrical resonance occurs, that is, if the contributing forms all have the same structure. Acetoacetic ester, for example, forms a resonance hybrid ion.



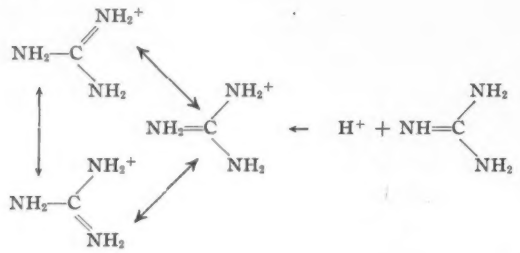
Symmetrical resonance is illustrated by the nitrate ion.



Conversely, if the elimination of a proton from an acid results in the loss of symmetrical resonance its ejection

[7] HALL AND SPRINKLE, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

is hindered and the substance is weaker in acidity (the conjugate base is a stronger base) than would otherwise be the case. This situation is illustrated by guanidinium ion which is neutral (*i. e.*, guanidine is a strong base).

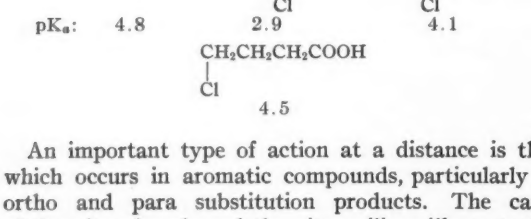


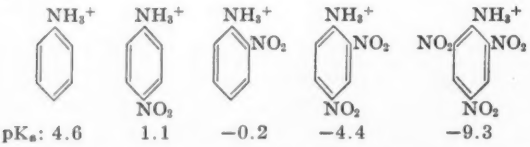
THE ACTION OF ACIDIFYING GROUPS AT A DISTANCE. VINYLOGY

Not only do acidifying groups function when substituted directly into water, for example, but they may also enhance the acidity of a substituted water when introduced into the substituent already present. Thus, in carboxylic acids (acylated water), the introduction of acidifying groups into the α-position markedly heightens the acidity. This effect falls off rapidly with the displacement of the acidifying group from the acidic hydroxyl.

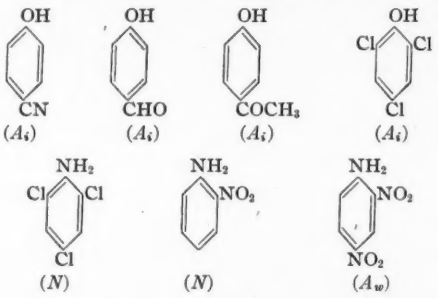
	CH_3COOH	$CH_2ClCOOH$	$CHCl_2COOH$
pK_a:	4.8	2.9	1.3
		CCl_3COOH	
		0.7	
	$CH_3CH_2CH_2COOH$	$CH_3CH_2CHCOOH$	CH_3CHCH_2COOH
		Cl	Cl
pK_a:	4.8	2.9	4.1
		$CH_2CH_2CH_2COOH$	
		Cl	
		4.5	

An important type of action at a distance is that which occurs in aromatic compounds, particularly in ortho and para substitution products. The cases of the nitrophenols and the nitroanilines illustrate the





principle of vinylogy,[8] according to which the vinylene group, —CH=CH—, acts as a good conductor of influences so that a molecule, X—CH=CH—Y, behaves like X—Y although with lowered intensity. This is due to the fact that if the possibility of resonance occurs in X—Y it will also occur in X—CH=CH—Y. The conjugated system of two vinylene groups, —CH=CH—CH=CH—, functions similarly. In the benzene ring a closed circuit of three vinylene groups permits cumulative effects such as those observed in picric acid and trinitroaniline. An examination of pK_a values discloses a remarkable additivity of acidifying effects of successive nitro groups. The result of this situation is that many phenols, though they bear a label which implies weak acidity, are intermediate or even strong acids, while some aromatic amines fail to exert the basicity found in aniline, and may actually be weak acids. Further examples are given below.



SALTS AND NEUTRALIZATION

In their current use, the terms *acid* and *base* apply, as has been shown, not merely to uncharged substances such as acetic acid, phenol, and aniline, but also to cationic acids such as methylammonium ion and to anionic bases such as benzoate ion. Consequently the terms *salt* and *neutralization* have lost their classical connotations completely. A *salt* may now be defined as a substance which, in the solid state, possesses an ionic lattice; that is, a substance which consists of oppositely charged ions held together by coulomb forces. The ions of a salt may be acidic, basic, or neutral substances. The term *neutralization* refers to a reaction in which a proton migrates from one base to another. In this usage the term is misleading and should be replaced by the term *acid-base reaction*. Acid-base reactions may occur in numerous successive steps and the question as to whether the products are neutral depends only on whether they constitute conjugate acids of acid-base systems of pK_a less than 12 to 13 or conjugate bases of acid-base systems of pK_a greater than 1 to 2. A study of the following series of reactions should prove illuminating, since it indicates how a proton may enter into a number of acid-base transfers before settling down in a non-acidic molecule. Assume first that benzenesulfonic acid is dissolved in water.

$$\underset{(A_s)}{C_6H_5SO_3H} + \underset{(N)}{H_2O} \rightarrow \underset{(A_s)}{H_3O^+} + \underset{(N)}{C_6H_5SO_3^-}$$

To this solution sodium acetate is added. Na^+ is a neutral substance. The following reaction occurs.

$$\underset{(A_s)}{H_3O^+} + \underset{(B_w)}{CH_3COO^-} \rightleftharpoons \underset{(A_i)}{CH_3COOH} + \underset{(N)}{H_2O}$$

[8] FUSON, *Chem. Rev.*, **16**, 1 (1935).

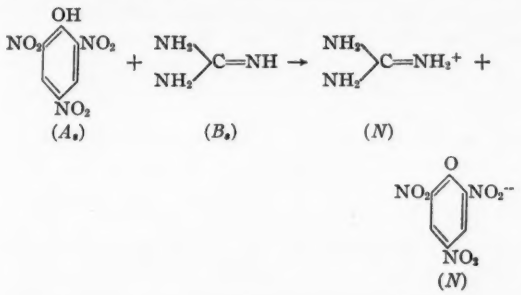
Then sodium phenolate is added. The following reaction occurs.

$$\underset{(A_4)}{CH_3COOH} + \underset{(B_4)}{C_6H_5O^-} \rightleftharpoons \underset{(A_w)}{C_6H_5OH} + \underset{(B_w)}{CH_3COO^-}$$

Finally sodium hydroxide is added causing the reaction

$$\underset{(A_w)}{C_6H_5OH} + \underset{(B_s)}{OH^-} \rightleftharpoons \underset{(N)}{H_2O} + \underset{(B_4)}{C_6H_5O^-}$$

Each of the foregoing reactions is a "neutralization" although in no case are both products *neutral* substances. Only when a strong base reacts with a strong acid does this result. For example, when guanidine (B_s) reacts with picric acid (A_s) guanidinium picrate (N,N) is formed.



(A_s) (B_s) (N) (N)

QUANTITATIVE TREATMENT OF ACID-BASE REACTIONS

The qualitative statements concerning acid-base reactions made in the previous section may be fortified by considering the matter quantitatively. This will be facilitated by reference to Figures 1 and 2.

Example 1. Suppose that the conjugate acid, $Acid_1$, of an acid-base system ($pK_a = 4.8$) is treated with one equivalent of the conjugate base, $Base_2$, of a second acid-base system ($pK_a = 9.4$). The two *pH–per cent conjugate base* curves have midpoints at pH 4.8 and 9.4, respectively. Since equivalent quantities of $Acid_1$ and $Base_2$ are employed, equilibrium will occur at a pH midway between 4.8 and 9.4 or 7.1. Inspection of the curves (Figure 1) indicates that at this pH practically all of the first acid-base system is present as conjugate base while practically all of the second is present as conjugate acid. Substituting in the fundamental equation

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

$$4.8 = 7.1 - \log \frac{[A^-]}{[HA]}$$

$$\log \frac{[A^-]}{[HA]} = 2.3$$

$$\frac{[A^-]}{[HA]} = \frac{200}{1}$$

That is, $^{200}/_{201}$ or 99.5 per cent of $Acid_1$ has been converted to $Base_1$ and vice versa for the second system, since there

$$9.4 = 7.1 - \log \frac{[A^-]}{[HA]}$$

$$\log \frac{[A^-]}{[HA]} = -2.3 = \bar{3}.7$$

$$\frac{[A^-]}{[HA]} = \frac{5}{1000}$$

That is, only $^{5}/_{1005}$ or 0.5 per cent of $Base_2$ remains unconverted to $Acid_2$. This example actually represents the case of benzoic acid–ethanolamine.

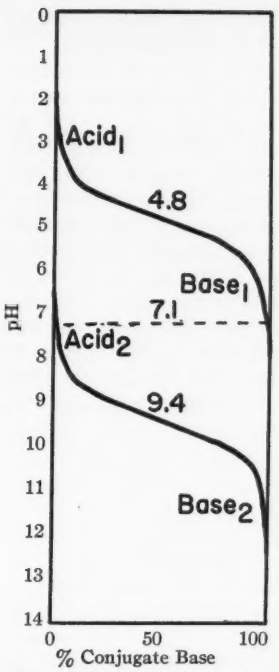


FIGURE 1.—INTERACTION OF $Acid_1$ ($pK_a = 4.8$) WITH $Base_2$ ($pK_a = 9.4$)

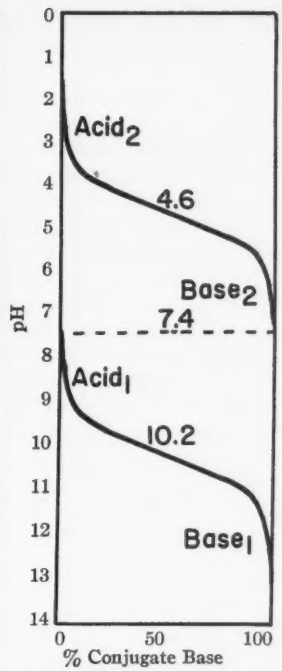


FIGURE 2.—INTERACTION OF $Acid_1$ ($pK_a = 10.2$) AND $Base_2$ ($pK_a = 4.6$)

Example 2. $Acid_1$ ($pK_a = 10.2$) is treated with an equivalent of $Base_2$ ($pK_a = 4.6$). Equilibrium occurs at pH 7.4 at which for the first acid-base system

$$10.2 = 7.4 - \log \frac{[A^-]}{[HA]}$$

$$\log \frac{[A^-]}{[HA]} = -2.8 = \bar{3}.2$$

$$\frac{[A^-]}{[HA]} = \frac{16}{10000}$$

Hence, only $^{16}/_{10016}$ or less than 0.2 per cent of the substances have interacted. In other words, practically no reaction has occurred. This example represents the case of *p*-cresol–*p*-toluidine (Figure 2).

Example 3. Acetic acid ($pK_a = 4.8$) is treated with an equivalent of *p*-toluidine ($pK_a = 4.6$) in dilute aqueous solution. Equilibrium occurs at pH 4.7

$$4.8 = 4.7 - \log \frac{[A^-]}{[HA]}$$

$$\log \frac{[A^-]}{[HA]} = -0.1 = \bar{1}.9$$

$$\frac{[A^-]}{[HA]} = \frac{8}{10}$$

Hence, the fraction of acetic acid converted to acetate ion is $^{8}/_{18}$ or 44 per cent.

COMPOUNDS CONTAINING ACIDIC AND BASIC GROUPS

An estimate of the acid-base character of compounds containing acidic and basic groups may be obtained by utilizing the relationship between the

strengths of conjugate acids and bases given in Table 1. The procedure to be followed involves four steps: (1) write the structure of the compound in its uncharged form; (2) classify the acidic and basic groups, assuming no interaction between the groups; (3) rewrite the structure after transferring protons from acidic to basic groups in the order of strengths, that is, first from strong acids and then from intermediate and weak acids in turn, and first to strong bases and then to intermediate and weak bases in turn; (4) classify the resulting charged acids and bases (see Table 1). If there is a decline in the number or the strengths of the acids *and* bases in passing from the original to the final structure then the latter structure is the stable one. If there is an increase, then the original structure is the stable one. If there is no change, the result is ambiguous and both forms may coexist in solution.

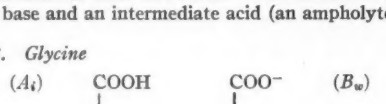
Example 1. Sulfanilic Acid

Since a strong acid ($ArSO_3H$) gives rise to an intermediate acid ($ArNH_3^+$) and a weak base ($ArNH_2$) to a neutral substance ($ArSO_3^-$), the second structure is the stable one and sulfanilic acid functions only as an intermediate acid comparable to acetic acid.

Example 2. p-Aminophenol

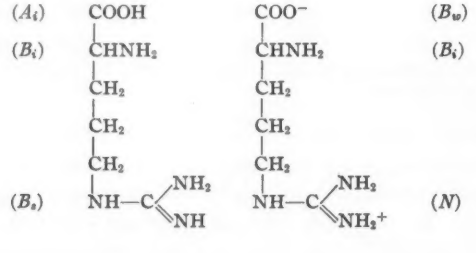
Since a weak acid would give rise to an intermediate acid and a weak base to an intermediate base, the uncharged form is stable and proton transfer does not occur. The substance functions as a weak base and an intermediate acid (an ampholyte).

Example 3. Glycine



The dipolar is the stable form and the substance functions as a weak base and a weak acid (an ampholyte).

Example 4. Arginine



The dipolar ion is stable and the substance functions as an intermediate base.

ACIDS AND BASES BROADLY DEFINED

In the broadest sense an *acid* is defined as a molecular or ionic species which, by reason of the presence of an atom whose valence shell lacks one or more pairs of electrons of the stable structure (duet, octet, decet, dodecet, etc.) is capable of adding to other species which possess one or more lone pairs of electrons. The latter species are known as *bases*.[9]

Some examples of acids and bases thus defined are:

Acids	
Halides of metalloids	BF_3, $AlCl_3$, $SnCl_4$, $FeCl_3$
Oxides of non-metals and metalloids	CO_2, SO_3, NO_2, Sb_2O_3
Cations of certain metals and hydrogen	Ag^+, Hg^{++}, Fe^{+++}, H^+
Carbonium ions	Ar_3C^+
Carbonyl compounds	Phenanthraquinone, benzil
Bases	
Anions, generally	Cl^-, NO_2^-, CH_3COO^-, OH^-, NH_2^-, ϕ_3C^-
Derivatives of water and ammonia	H_2O, ROH, R_2O, R_3N, RCONH$_2$, RCOR

Acid-Base Reactions

("Neutralizations")

$$H^+ + OH^- \rightarrow H_2O$$
$$BF_3 + NR_3 \rightarrow F_3B{:}NR_3$$
$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$

PRIMARY AND SECONDARY ACIDS AND BASES

Most acid-base reactions are instantaneous at all temperatures which have been studied. In some cases, however, the reaction has a measurable rate which increases with rising temperature indicating that the molecules of the acid or the base require activation before they react. Such substances are known as *secondary* acids and bases. An example of a secondary acid is nitromethane, which in $N/16$ solution requires fifteen minutes to react with $N/16$ barium hydroxide at 0°C.[10] Carbon dioxide also reacts only slowly with hydroxyl ion to form bicarbonate ion.

$$CO_2 + OH^- \rightarrow HCO_3^-$$

The admission of such species to the categories of acids and bases opens the way for organic structural types such as acid halides, acid anhydrides, and esters to be considered as acids, since like other acids they are capable of reacting with bases (say, hydroxyl ion or ammonia), albeit more or less slowly. In practice, it may even be difficult to distinguish an ester such as methyl oxalate from a carboxylic acid, since it reacts rapidly enough with hydroxyl ion or ammonia to be directly titrated.

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[9] (*a*) Lewis, *J. Franklin Inst.*, **226**, 293 (1938); (*b*) Luder *Chem. Rev.*, **27**, 547 (1940).

[10] Hantzch and Veit, *Ber.*, **32**, 618 (1899).

Nitrogen Fixation

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FREE NITROGEN AND FIXED NITROGEN

THE surface of the earth is at the bottom of an atmospheric ocean some hundreds of miles deep. This atmosphere is made up almost entirely of a mixture of two gases, oxygen and nitrogen, the latter constituting about four-fifths of the mixture. Inasmuch as life originated and evolved at the interface between the atmosphere and the earth, it would be strange indeed if living matter did not reveal in its composition something of the environment which fostered it. Actually, we find that oxygen, nitrogen, water, and a score or more of the common elements of the earth's surface are necessary to maintain living organisms.

Nitrogen, as an inert component of the earth's atmosphere, was recognized early in the development of chemistry. Its chemical inactivity, as compared with that of other elements, impressed the early chemists. The French chemist Lavoisier called the element "azote," meaning "lifeless." As knowledge of the composition of materials grew, it must have surprised chemists to find that nitrogen is one of the chemical components of so many things. All living organisms, both animal and plant, were found to contain nitrogen in chemical combinations; ammonia, urea, nitric acid, saltpeter, sal ammoniac, and a large number of other chemicals known to early chemists were eventually found to be nitrogen-containing compounds. All fertile soils were found to contain nitrogen compounds. More and more it came to be recognized that, although the free nitrogen of the atmosphere is a relatively inert element, nevertheless the element nitrogen, in chemically combined form, plays a most important role both in the animate and the inanimate world. As knowledge of the role of nitrogen grew, it puzzled chemists that there was seemingly no link between the great reservoir of free nitrogen in the air and the chemically combined nitrogen found in all plants and animals. It was shown early in the nineteenth century that plants assimilate nitrogen compounds from the soil, and the value of nitrogenous materials as fertilizers came to be recognized and understood. Nevertheless, the question of the source of the supply of nitrogen compounds in the soil remained unanswered, for the nitrogen content of an unfertilized field did not decrease nearly as rapidly as it should when nitrogen-carrying crops were removed year after year from the field.

HOW THE FIXED NITROGEN SUPPLY OF THE SOIL IS MAINTAINED

Liebig, who carried out his magnificent researches in agricultural chemistry in early decades of the nineteenth century, rightly postulated that the nitrogen found in soil could only come from the atmosphere. Observing that rain water always contains a little ammonia, and knowing that ammonia gas is invariably one of the decomposition products of decaying plants and animals, he advanced an explanation of soil nitrogen supply which, although true, eventually proved to be only a very small segment of the whole truth. Liebig visualized a great, natural "ammonia cycle," wherein decaying vegetable and animal matter release ammonia to the atmosphere. This ammonia is later dissolved in rain and returned to the soil, there combining with acidic compounds in the soil to form ammonium salts. Plants assimilate nitrogen compounds from the soil. Herbivorous animals obtain their nitrogen from the plants on which they feed, and carnivorous animals obviously secure nitrogen from their nitrogen-carrying foods. But generations of plants and animals die and decay, and the nitrogen of their bodies returns either to the soil, or, as ammonia, to the atmosphere, again to be recaptured in rain water.

So thought Liebig a hundred years ago. The ammonia cycle from the atmosphere to plants, to animals, and thence back to the soil and the atmosphere actually takes place, but the soil is by no means wholly dependent on this cycle for its ever-renewed supply of nitrogen compounds. Long after Liebig's day it was discovered that there are minute organisms living in the soil which, curiously, are able to assimilate free nitrogen directly from the air and, in their life processes, convert it to nitrogen compounds. These "nitrogen-fixing" bacteria are of two sorts, namely those which live free in the soil and those which live only in colonies on the roots of certain plants known as "legumes." Clover, bean, pea, vetch, alfalfa, and lespedesa are among the members of the legume family, and are of great importance in agriculture, not only because these plants are themselves rich in nitrogen, but also because they increase the nitrogen content of the soil in which they grow.

In these nitrogen-fixing bacteria we have, indeed, the link between the enormous reservoir of free nitrogen in the atmosphere and all the living plants and animals of the earth. To be sure, man has in recent decades learned how to "fix" the free nitrogen of the air as nitrogen compounds by chemical processes and thus to supplement, in a feeble way, the nitrogen supplied to the soil by the natural processes.

How the nitrogen-fixing bacteria fix nitrogen is not known, even today. All the processes that man has invented to fix nitrogen use high temperatures and often high pressures also. The chemistry used by the bacteria is certainly quite different from the drastic sort employed by man.

THE GROWING DEMAND FOR NITROGEN COMPOUNDS

Nitrogenous materials were used as fertilizers long

before such materials were recognized as carriers of fixed nitrogen. Likewise, gunpowder, of which potassium nitrate is a component, came into use long before the chemistry of its manufacture or use was understood. The agricultural demand for nitrogenous fertilizers increased as certain areas of the earth became more densely populated, and, in particular, it increased rapidly after the role of nitrogen in agriculture became known about a hundred years ago. Likewise, the demand for gunpowder grew as armies grew in size and number. Almost any nitrogenous material would serve as a fertilizer, but for the manufacture of gunpowder the demand was specifically for potassium nitrate. The earth was ransacked for a supply of potassium nitrate—or "saltpeter," as it was called. Only small deposits were found, but about a hundred years ago the natural sodium nitrate deposits in Chile were located. Thereafter "Chilean nitrate" was used in agriculture and eventually a large nitrate industry developed in Chile.

The development of a coke industry also made available to agriculture a supplementary supply of nitrogenous fertilizer, for in making coal gas and coke from coal, ammonia is obtained as a co-product, and this ammonia may be converted readily to fertilizer salts.

The demand for potassium nitrate for gunpowder was not adequately met until after the middle of the nineteenth century when the potash mines near Stassfurt, Germany, were opened. Then, for the first time, an adequate supply of potassium chloride became available. By reaction between potassium chloride and sodium nitrate, the desired potassium nitrate was readily manufactured.

The nineteenth century witnessed not only a rapid expansion in agriculture but also a rapid development of industry. Industrial demands for nitrogen compounds, such as ammonia, nitrates of various kinds, ammonium salts, nitrogen-containing dyes, high explosives, etc., were added to the increasing nitrogen requirements of agriculture and to the military needs. In spite of the new sources of supply, such as the Chilean deposits of sodium nitrate and the coal carbonizing industry, a more or less chronic shortage of nitrogen compounds developed. The amount of by-product ammonia available from the coking of coal was obviously limited by the amount of coke needed in industry. The Chilean nitrate industry became a monopoly, politically controlled by the Chilean government which placed a heavy export duty on the nitrate, and economically controlled by British capital which demanded and obtained an excessively high profit. The monopoly was irksome to all users of nitrate and, as is always the case, created a powerful incentive for the discovery of means of relief. An obvious solution of the problem was to find practical methods of "fixing" the free nitrogen of the atmosphere, *i. e.*, chemical methods by which the free nitrogen could be induced to enter into combination with other elements to form nitrogen compounds.

THE ARC METHOD OF NITROGEN FIXATION

As early as 1772 the English chemist, Priestley, had discovered the "arc method" (electric spark) of fixing nitrogen but he did not understand the chemistry of his discovery. In 1774, Cavendish observed that when an electric arc (spark) was passed through a mixture of five volumes of oxygen mixed with three volumes of air, the gases united to form a gas which was soluble in an alkaline solution. This method of fixing nitrogen was of no commercial importance, however, because electrical energy could be produced at that time only by prohibitively expensive methods. By the end of the nineteenth century this situation had changed. The transformation of mechanical energy into electrical energy by highly efficient machines had been developed, and hydroelectric plants utilizing the mechanical energy of falling water had been built. The stage was set for a successful arc process of nitrogen fixation.

Two Americans, Bradley and Lovejoy, built the first commercial plant using the arc method at Niagara Falls in 1902. The venture was not profitable, but was a distinct advance in the art. A few years later commercially successful plants were built in Norway, using an arc method developed by the physicist Birkeland and the engineer Eyde.

The chemistry of the arc method of nitrogen fixation is relatively simple. The difficulties lie in the technology of putting the chemical reaction to practical use. When a nitrogen-oxygen mixture, such as that which constitutes the atmosphere, is heated, a small portion of the gases unite to form nitric oxide, thus:

$$N_2 + O_2 \rightleftarrows 2NO$$

The reversed arrows used in the above expression indicate that the reaction moves to the right or to the left as conditions change. All chemical reactions are actually of this nature, but in many cases the conditions are such as to favor the reaction in one direction so overwhelmingly that chemists ordinarily need not consider both reactions. In the present instance, however, the process can be understood only by considering both the forward and reverse reactions as represented in the equilibrium expression written above.

At ordinary temperatures the equilibrium between free nitrogen and free oxygen on the one hand and nitric oxide on the other is such that practically no nitric oxide may be detected in the mixture. At the extremely high temperature of the electric arc, the reaction proceeds a short measure to the right, and a small percentage of nitric oxide appears in the hot mixture of gases. If, now, the gases are allowed to cool slowly, the reaction moves to the left until practically no nitric oxide remains. An arc process may therefore appear to be a useless procedure, for in the end only the original uncombined gas remains. Here is where the trick comes in which makes the arc process practical.

The chemical expression written above does not indicate anything as to the *rate* at which the reactions may move to right or left. It is well known that most chemical reactions speed up as the temperature of the

reactants is raised, and slow down as the temperature falls. At the very high temperature of the electric arc, one would expect that any reaction which could take place under such conditions would take place quickly. The trick in the arc method is to remove the very hot gas mixture from the arc and to chill the mixture very rapidly by diluting it with a large proportion of air at ordinary temperature. The sudden cooling slows up the reverse reaction, *i. e.*, the decomposition of the nitric oxide, until the reaction practically ceases and a mixture of air carrying one to two per cent of nitric oxide is obtained. The nitric oxide does not remain as such in the mixture, for as the temperature falls below about 600°C. another equilibrium reaction sets in. This reaction may be represented most simply by the expression

$$2NO + O_2 \rightleftarrows 2NO_2$$

In the arc process the cooled gases from the arc are brought into contact with water in absorption towers. Here the nitrogen peroxide (NO_2) reacts with water, thus:

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$$

It will be noted that for every three molecules of NO_2 which react with water, one molecule of NO is released. This NO will then react with the oxygen present in the large excess of air in the gas mixture, again forming NO_2. Unfortunately the reaction:

$$2NO + O_2 \rightleftarrows 2NO_2$$

moves to the right rather slowly under the conditions which exist in the absorption tower. Because the proportion of NO in the gas mixture coming from the arc is so small, and because the reactions in the absorption tower are so slow, very large and therefore very costly absorption towers are required. Furthermore, the efficiency of the arc as a method of fixing nitrogen is very low. Most of the electrical energy is used to heat the gas mixture in the arc and not to form the small proportion of nitric oxide obtained. Therefore this method can be used only where large amounts of electrical energy can be produced economically, and where such energy cannot find more profitable uses. It was for this reason that the arc process plants were located in Norway where hydroelectric energy could be produced cheaply and where no large industries were located at the time the arc plants were built.

In the Norwegian arc process plants, the nitric acid from the absorption towers was neutralized with lime to form calcium nitrate. This "Norwegian nitrate" absorbs moisture readily from moist air and cakes badly. It was therefore packed in tight wooden kegs for the market. It was sold as a fertilizer and was rather widely used for several years. The arc method of fixing nitrogen was applied in a few small plants located elsewhere than in Norway, but was eventually replaced, even in Norway, by more economical methods.

THE FIXATION OF NITROGEN AS A CYANIDE

Another method of fixing nitrogen was familiar to chemists more than one hundred years ago. As early as 1842 attempts were made to establish commercial scale nitrogen-fixing plants using the so-called cyanide method. It had been discovered in 1828 that when nitrogen is brought into contact with a hot mixture of an alkali carbonate and carbon in an iron tube, an alkali cyanide is formed. Early attempts to use this method failed. During World War I, further trials of the method were made, but the small plants that were built soon were abandoned.

THE CYANAMIDE METHOD OF NITROGEN FIXATION

The cyanamide method of nitrogen fixation was discovered by Frank and Caro in the closing decade of the nineteenth century. In studying nitrogen fixation by the cyanide method, it was found that nitrogen would combine with certain metal carbides to form both cyanides and cyanamides. With calcium carbide at about 1000°C., the product was almost entirely calcium cyanamide. Later it was found that calcium cyanamide may be used directly as a nitrogen-carrying fertilizer.

Factories using the new method of nitrogen fixation were built in Germany, Italy, and elsewhere in the period 1905–10. In 1908 a plant using this method was built by the American Cyanamid Company on the Canadian side of Niagara Falls.

In the cyanamide process, coke and lime are heated in an electric furnace to form calcium carbide, thus:

$$3C + CaO \rightleftarrows CaC_2 + CO$$

The calcium carbide removed from the electric furnace is cooled, ground, placed in small cylindrical ovens, and treated with nitrogen gas at a temperature of about 1000°C. The nitrogen may be obtained by liquefying air at low temperatures and separating the nitrogen from the oxygen. Under the conditions in the ovens, the nitrogen reacts slowly with the calcium carbide to form calcium cyanamide, thus:

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C$$

The cyanamide mixed with the carbon formed in the reaction is removed from the ovens as a solid cake. It is then ground, oiled to reduce its dustiness (or granulated), and sold as a fertilizer. Its use as a fertilizer is somewhat handicapped by the fact that it is dusty, even after oiling or granulating, and it is alkaline and toxic. It is still manufactured on a fairly large scale and used in agriculture and for other purposes, but it appears probable that the cyanamide method will eventually be abandoned as was the arc method of nitrogen fixation.

THE DIRECT SYNTHETIC AMMONIA METHOD OF NITROGEN FIXATION

A sound scientific foundation for the direct synthetic ammonia process was laid during the first decade of the present century. Equilibrium reactions, such as discussed in describing the arc method of nitrogen fixation, were coming to be more fully understood. It had long been suspected that an equilibrium existed between

hydrogen and nitrogen on the one hand and ammonia on the other, *i. e.*

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

Attempts to study this equilibrium did not yield much information, however. Hydrogen and nitrogen, when brought together under ordinary conditions, apparently formed no ammonia. Several investigators had, on the other hand, reported that the decomposition of ammonia was never quite complete when it was passed over hot solids or through hot iron tubes. The trace of ammonia remaining indicated that there might indeed be a truly reversible reaction such as represented by the expression written above.

The fact that no ammonia could be detected when hydrogen and nitrogen were brought together at ordinary temperatures could be explained on either of two assumptions, namely, (1) the equilibrium under ordinary conditions was such that the proportion of ammonia was too small to be detected, or, (2) the reaction between hydrogen and nitrogen was so slow under ordinary conditions that not enough ammonia was formed during the experiment to be detected by chemical methods. That this latter hypothesis was the correct one was indicated by the fact that when ammonia was passed through a hot iron tube, enough still remained undecomposed to be detected chemically. Finally, early in the present century, the German chemist Fritz Haber and his research students undertook a prolonged study of the reaction.

The equilibrium was a difficult one to study. If the reaction between hydrogen and nitrogen were really extremely slow at ordinary temperature, then it was natural to try measurements at higher temperatures. This in itself was difficult but not the only difficulty. It happens that higher temperatures favor the right-to-left reaction written above, *i. e.*, the already small proportion of ammonia present when the two reactions are in equilibrium is decreased almost to the vanishing point. High pressure, however, favors the left-to-right reaction. This is the result of the fact that *three* molecules of hydrogen combine with *one* of nitrogen to form *two* of ammonia gas. It is a well-known principle that equal numbers of molecules of different gases occupy the same volumes—at the same conditions—and hence the ammonia has only half the volume of the hydrogen-nitrogen mixture. The "squeezing together" effect of pressure favors this reduction in volume, and therefore the formation of ammonia.

The technic of working at high pressures was not highly developed forty years ago. However, Haber and his students were eventually able to overcome all the difficulties and to measure with considerable accuracy the proportions of hydrogen, nitrogen, and ammonia present under various conditions of temperature and pressure. Catalysts were found which would accelerate the combination of hydrogen and nitrogen. Professor Nernst, another German chemist, was at this time engaged in the study of gaseous reactions under pressure, and the technic which he developed was no doubt of value in the studies which Professor Haber and his students had undertaken.

With the catalysts which had been discovered, and with an accurate knowledge of the equilibrium involved, it began to appear that a practical process of nitrogen fixation might be developed. In 1908 the Badische Anilin-und Soda Fabrik undertook this task. The technical difficulties involved were obviously great, but the German company had at its command great resources in the way of chemical and engineering talent as well as in funds.

The first synthetic ammonia plant in the world was put into operation at Oppau, Germany, in 1913. Then came World War I and the blockade of Germany. A stock pile of Chilean nitrate had been accumulated in Germany for what was intended to be a short war. Cut off from imports of Chilean nitrate, and with no end of the war in sight, it was imperative that synthetic nitrogen production in Germany be increased greatly in order to meet the enormous military demand for explosives, all of which are nitrogen compounds. The existing cyanamide plants were expanded and a few small arc plants were set up, but the power requirements of these processes were so high that they could not meet Germany's need for fixed nitrogen. Under these conditions, the synthetic ammonia plant at Oppau was expanded greatly and eventually a very large synthetic ammonia plant was built near Merseburg. Thus Germany solved her nitrogen problem, and the synthetic ammonia process developed with unusual rapidity.

After World War I, synthetic ammonia plants were built in many countries. By 1926 the Chilean monopoly was completely broken, and the price level of nitrogen products now is fixed by the cost of making synthetic ammonia.

All synthetic ammonia plants are alike in utilizing catalysts to establish an equilibrium between hydrogen, nitrogen, and ammonia. The plants differ greatly in other respects. Many catalysts have been discovered; the one most commonly used is the magnetic oxide of iron (Fe_3O_4) into which are incorporated small amounts of other compounds, called "promoters." Alumina (Al_2O_3) and potassium oxide (K_2O) are the promoters most commonly used.

Hydrogen may be prepared in many ways. The original German plant used the water gas method. Other plants use coke-oven gas. Some plants use electrolytic hydrogen and some use the gases obtained from the thermal decomposition (cracking) of oil or natural gas. All plants naturally use nitrogen from the air. In all cases the hydrogen-nitrogen mixture must be thoroughly purified, and in most plants the equipment for this step in the process is the major portion of the plant. Various methods are used in purifying the hydrogen-nitrogen gas mixture and plants differ in both method and equipment used.

As mentioned above, pressure favors the synthesis of ammonia from nitrogen and hydrogen. Plants have been built to operate at various pressures in the range

from 100 atmospheres to 900 atmospheres. The present trend appears to be toward use of pressures in the neighborhood of 350 atmospheres (about 5150 lb. per sq. in.). In all plants, the purified mixture of hydrogen and nitrogen is passed through a bed of catalyst material. The proportion of ammonia in the gas issuing from the catalyst chamber depends on the temperature and pressure maintained in the catalyst chamber. The ammonia in the mixture is removed, usually by refrigeration, and the remaining gases are returned to the system, mixed with additional hydrogen-nitrogen gas, and passed again through the catalyst.

HUGO RUDOLPH KRUYT

(Frontispiece)

ALTHOUGH the foundations of colloid chemistry go back to the time of Francesco Selmi, nearly a hundred years ago, it was not until Graham, in 1861, invented the term "colloid" that this branch of chemistry made its formal entry into the scientific world. With the introduction of Zsigmondy's ultramicroscope a new era was ushered in with which the names of Perrin, Svedberg, Wolfgang Ostwald, and Herbert Freundlich are connected. Freundlich's "Capillary and Colloid Chemistry," first published in 1910, exerted a powerful influence in converting Kruyt from a phase rule chemist into a devotee of the chemistry of colloids. Thirty years of intensive cultivation of this field resulted in more than a hundred publications by Kruyt and his pupils. In addition to numerous journal articles Kruyt has written an "Introduction to Physical and Colloid Chemistry," published in six Dutch, one German, and one Russian editions, and a well-known textbook on Colloids of which two English and one French editions have been issued.

An accomplished linguist, Kruyt has been a frequent speaker at international meetings and he is equally well known on both sides of the Atlantic. In the spring of 1927 he came to America, where he visited a number of universities and colleges. He attended the fifth annual Symposium on Colloids at Ann Arbor in June, 1927, as guest speaker and spent the summer of that year as visiting professor at the University of Michigan.

A promoter of amity among scientists in the period following the peace of Versailles, Kruyt, being a native of a then neutral country (Holland), was ideally fitted by training and by temperament to re-establish the ties severed by four years of bitter warfare. A preliminary meeting at Utrecht in June, 1922, arranged by Kruyt and his colleagues, Cohen and van Romburgh, was followed by other equally successful gatherings and paved the way for the establishment of the Union internationale de Chimie at Liège in 1930.

Within the borders of his own country Kruyt has been active in many extrascholastic affairs. Brought up in a religious atmosphere, he maintained throughout his student days and later his interest in the student Y. M. C. A. in Holland. An ardent believer in close coöperation between science and industry, he has not only taken part in the development of Dutch industries as chemical adviser and consultant but in several public addresses and a number of pamphlets has made valiant efforts to influence public opinion and governmental authorities toward abolishing the rigid separation of pure and applied science.

Hugo Kruyt was born in Amsterdam in 1882, the youngest of five children of the printer, bookseller, and publisher, J. H. Kruyt, and Maria Perkins, daughter of an English chemist who, later on, became a school principal in London. During his high-school days at Amersfoort, Kruyt early showed his predilection for chemistry. A sign over the door to an attic notified the general public of the location of Kruyt's "chemical, physical, and optical laboratory." In 1900 he entered the University of Amsterdam where he studied physics under van der Waals and chemistry under Bakhuis Roozeboom, the successor of van't Hoff and at that time the chief exponent of phase rule chemistry. After the untimely death of Roozeboom in 1907 Kruyt, unwilling to continue the work for his doctor's thesis under Roozeboom's successor Smits, went to Utrecht to finish his studies at the van't Hoff laboratory. The following year he obtained his Ph.D. with Ernst Cohen as promoter. The bonds of uninterrupted friendship and coöperation between professor and student, later colleague, and finally successor, are too well known to dwell upon. Kruyt's phase rule studies, as exemplified by his doctor's thesis on the dynamic allotropy of sulfur, followed by a similar study on selenium, brought him in contact with Tammann (in Göttingen) whose methods of thermal analysis he investigated in the summer of 1910. Appointed to an assistantship in 1909 and three years later to a lecturership in phase rule, Kruyt continued, in collaboration with Cohen, his studies on the standard cadmium cell first begun in 1908. Gradually his interests shifted to the field of colloids and 1912 found him in Freundlich's laboratory where he became acquainted with the ultramicroscope as a tool in colloid-chemical research. The year 1916 brought his appointment as assistant professor (or extraordinarius) in physical chemistry, from which position he was advanced to full professor (ordinarius) in 1921. On the retirement of Cohen in 1939 Kruyt succeeded to the directorship of the van't Hoff laboratory.

Kruyt's contributions to colloid chemistry are many and some of these have already become so classic that they have found their way into elementary texts of physical chemistry. His early colloid-chemical investigations dealt with the stability of suspensoids, the effect of electrolytes on electrokinetic potential, flow potential, and electrophoresis, the nature and the composition of the electric double layer, the kinetics of flocculation, heat of adsorption, and lyotropy. In 1918 he started to attack the problem of the stability of hydrophilic sols, partly in collaboration with his pupil and later colleague Bungenberg de Jong. Electro-viscous effect, solvation, and coacervation were some of the phenomena drawn upon to explain the nature of lyophilic colloids. These studies enabled Kruyt to bridge the gap between lyophobic and lyophilic sols. His concept of the unity in the theory of colloids as presented in a number of public lectures has found widespread acceptance.

The reputation gained in his chosen field has brought to Kruyt honorary membership in the Dutch and in the Roumanian Chemical Societies and several tempting offers from other universities both here and abroad which he has consistently declined. Being charged, in the present academic year, with the added duties of *rector magnificus* of the University of Utrecht, Kruyt carries on, after sixty years of active life, under most trying circumstances with the silent and serene fortitude of a true philosopher and the unshakable belief in the return of sanity among men and among nations.

—Contributed by H. S. van Klooster, Rensselaer Polytechnic Institute

● The Pittsburgh Plate Glass Company has recently issued an excellent pamphlet entitled "Glass and Its Adaptability to Modern Needs," which is principally devoted to a discussion of the various ways in which glass can be made to substitute for other more strategic materials in the present emergency.

Chemistry Teachers and the War

AUSTIN M. PATTERSON *Washington, D. C.*

TEACHERS of chemistry and of other scientific and technical subjects are wondering these days how they can make the best contribution to their country at war. Many, perhaps, feel a sense of frustration because, as they think, they are not engaged directly in the war effort. They are asking what they and their institutions can do to help in the emergency. The following impressions of one chemist on the subject are offered for whatever they may be worth.

It is of first importance that we all realize that the regular processes of education must go on. They are going to be modified, yes; they may be greatly changed. But one thing is sure: The education of professional chemists, physicists, engineers, and other highly trained individuals on whom the conduct of modern war greatly depends must not be interrupted.

The first duty, then, of teachers of chemistry and chemical engineering is to see that their capable students are trained as thoroughly as ever and that secondary-school, undergraduate, and graduate work is continued at a high level of performance. In the movement for shortening the time to graduation the institutions have generally rejected any idea of curtailing the curriculum. The shortage of trained chemists is serious now and will grow worse. There is an increasing demand, not only for bachelors of science but for masters and doctors of philosophy on the one hand and for men with three, two, or even one year of college chemistry on the other. As a result of the demand, opportunities for women with chemical training are increasing, and it seems likely that they will soon be needed to replace men in positions that have not usually been open to them heretofore; in fact, this process has already begun.

Persons whose full time is absorbed in their regular scientific or technical teaching of either men or women in high school or college have good reason to believe that they are directly helping with the prosecution of the war, for there is no way of knowing how long it may last.

Such teachers also have an opportunity to influence the vocational choices of students who show aptitude for scientific studies. The urgent demand for chemists, laboratory technicians, physicists, engineers, supervisors, and physicians can be presented. There may be dislocations in some of these callings after the war is over, but it seems probable that we are headed toward a more technological type of civilization. This country will need larger numbers of technically educated men and women on various levels if it is to hold its own with strong competing nations, and their training must be more thorough than much of it has been in the past.

For those college teachers of chemistry who have time and facilities beyond their regular teaching work, opportunities are not wanting for usefulness. President Conant has described the work of the National Defense Research Committee, of which he is chairman.[1] This is engaging the services of many physicists, engineers, and chemists in research work. Engineering, Science, and Management Defense Training (ESMDT) of the U. S. Office of Education is sponsoring the giving of short, practical courses in chemistry, physics, engineering, and production supervision by more than 160 institutions over the country. These courses are outside the regular curriculum and are given chiefly in the evening to workers in war industries.

The change which is now going on and which, if we are correct, will continue after the war, will bring special pressure on the liberal arts colleges, as they are well aware. The writer is not one who wishes to see a liberal education discredited, or a greater proportion of young people cast in a narrow technical mold. There is an almost crying need for chemists and engineers who are better read, who can express themselves in better English, and who are better acquainted with broad human problems.

But there is no longer time for a large number of young men and women to indulge in a four-year period of dilettante education, following too often a superficial pre-college course. The high school must provide a solid foundation, either for vocations on a lower level or for college. The college must get down to business as a community of scholars, an intimate association of teachers and taught, and offer its students so much of varied but solid interest within its program that they will not be compelled to invent a whole outside program of their own, of less value. The liberal education must be there, for technical as well as other students, but it must be integrated with more direct training for one's life work. Otherwise, so rigorous are professional demands becoming that the chemist or doctor will be too old before he starts to practice.

For the present, at least, there should be more direction toward scientific and technical pursuits. There should be planned opportunity for practical experience as a part of the educational process. Those who are not fit material for college graduation should be shunted off at the end of high school or of junior college with the preparation for life best suited to them, while the more gifted should be given financial aid, if necessary, to permit them to go on, because the country needs them.

This dream of educators is not new, but it may be coming to pass sooner than we think. War is a great accelerator, and the colleges will have to adapt themselves quickly or suffer. Many of the changes forced by the war may turn out to be more or less permanent; it is high time to be planning ahead. Chemistry teachers need no persuasion, but they can help by discussing these trends with school authorities.

[1] *News Ed.*, **19**, 1237–8 (Nov. 25, 1941).

Sulfanilamide and Related Chemotherapeutic Agents

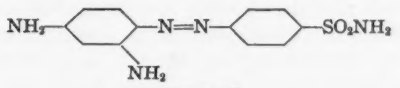
LAWRENCE H. AMUNDSEN *University of Connecticut, Storrs, Connecticut*

CHEMOTHERAPY is the treatment of internal disease by chemical reagents that have a toxic effect upon the pathogenic microörganism without seriously poisoning the patient. The use of the term is restricted ordinarily to synthetics. Ehrlich and the host of workers that followed him were quite successful in producing drugs to cure diseases caused by spirochetes and protozoa but almost no progress had been made against bacilli or cocci until the discovery and application of Prontosil by Mietzsch, Klarer, and Domagk.

The discovery of the action of Prontosil, sulfanilamide, and related compounds is one of the most important developments ever made in chemotherapy. Since some of the infections due to such lower forms of bacteria as bacilli and cocci at last have yielded to treatment with synthetic drugs, hope is held for the early conquest of the virus diseases. In laboratories all over the world the search is going on for drugs of this type that will be effective against still other infections and that will not give the serious toxic reactions sometimes caused by those now in use.

This development is not quite ten years old. It originated with the patenting of Prontosil in Germany in December, 1932. This patent was published in January, 1935, and in the following month Domagk published his famous paper describing the results of his tests of Prontosil on mice and rabbits. In the fall of the same year a group at the Pasteur Institute announced that a simpler compound, sulfanilamide, had the same protective and curative action as Prontosil. The unbelievably active research that followed Domagk's report is said to have been responsible in the next five years for the publication of the synthesis of about 1300 new derivatives of sulfanilamide. No one knows how many compounds have been made and tested but the number is larger than that disclosed in publications. Chemotherapeutic activity against bacteria has been found not only in the sulfonamides but also in certain sulfones, sulfoxides, sulfides, disulfides, arsinic acids, arsyloxides, arsines, phosphonous acids, phosphinous acids, phosphines, and even to a slight extent in *p*-nitrotoluene, *p*-nitrobenzoic acid, and a few related nitro compounds.

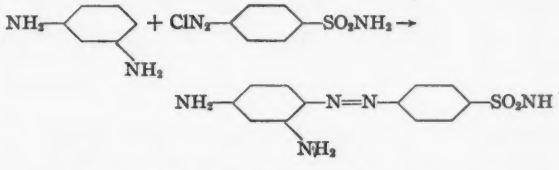
This class of drugs is effective against many of the diseases caused by hemolytic streptococci, pneumococci, meningococci, gonococci, staphylococci, and even certain diseases caused by other organisms. Erysipelas, gas gangrene, gonorrhea, meningitis, pneumonia, and puerperal fever are a few of the many that have reacted favorably. It has been stated that a critical review of reports on the chemotherapy of virus diseases shows that the sulfonamide compounds are effective against a few of them. There is some doubt, however, if the infecting agent in all these cases, for example in trachoma, can be classed as a true virus.

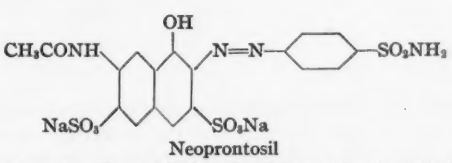


Prontosil
2,4-Diaminoazobenzene-4′-sulfonamide

Although Prontosil was the first of the sulfonamide drugs, it is not widely employed today. It never has been in common use in the United States. It was used clinically in Germany in 1933 and 1934 but it was Domagk's paper in 1935 reporting the curing of streptococcic infections in mice and rabbits that put Prontosil therapy on a sound scientific basis and attracted to it the attention of physicians and research workers throughout the world. Because of his pioneer work in the field Domagk was selected for the 1939 Nobel Prize in Physiology and Medicine although Hitler's decree prohibited his acceptance of it. Intensive research that began in France and England in 1935 and in the United States in 1936 has resulted in almost complete substitution for Prontosil of other drugs, notably sulfanilamide, sulfapyridine, sulfathiazole, and sulfadiazine, although some others have been used more in Europe.

Prontosil is made by coupling diazotized sulfanilamide with *m*-phenylenediamine; related azo compounds are made similarly. Possibly the effectiveness of Prontosil may be due entirely to sulfanilamide reformed from it within the animal body but the many experiments performed to test this theory have given evidence that is contradictory.





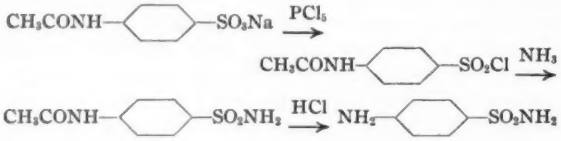
Neoprontosil
Disodium 2-(4-sulfonamidophenylazo)-7-acetylamino-1-hydroxynaphthalene-3,6-disulfonate

A great many azo compounds of the Prontosil type

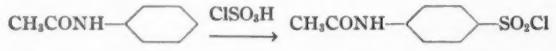
have been made but Neoprontosil is the only other one that has become well known. This compound and its beneficial action were announced in July, 1935, by Domagk. It has been called also Prontosil Soluble, Prontosil S, and even has been sold under the name of Prontosil. It is more soluble in water than is the original Prontosil and its solutions therefore have been used for injection.

Sulfanilamide

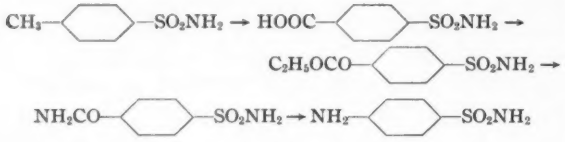
Sulfanilamide is the best known and most widely used member of the group. No doubt this is due in part to its ready availability at low cost. This compound and a relatively simple and cheap method for preparing it have been known since 1908, so it is not subject to control by patent. Gelmo described the original preparation of sulfanilamide by the following series of reactions.



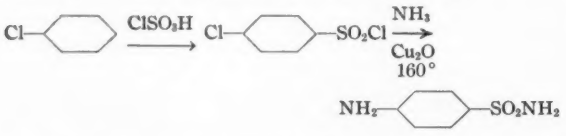
The only significant variation in this procedure today is the preparation of the acetylsulfanilyl chloride from



acetanilide and chlorosulfonic acid. Although it is impossible to say with certainty what methods are being used industrially, sulfanilamide probably is made essentially by Gelmo's method with the above modification. Another method of preparing sulfanilamide has been patented covering the following steps and certain modifications of them.

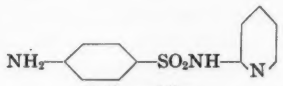


Still another method is found in a more recent patent describing the preparation of sulfanilamide from chlorobenzene and claiming coverage of the last step.



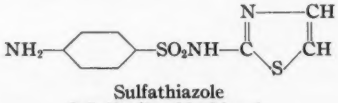
Sulfanilamide's therapeutic action was discovered by studying the effect of changes in the molecular structure of Prontosil. When modifications were made in the portion of the molecule to the left of the azo linkage as it is written above, little or no change was found in the chemotherapeutic activity of the compounds so produced. On the other hand, several compounds having structures different from Prontosil on the right of the azo linkage were inactive. The conclusion was drawn that it was only the latter portion of the Prontosil molecule that controlled chemotherapeutic activity and that Prontosil in the animal body was split at the azo linkage with the formation of sulfanilamide. As a first step in testing this hypothesis, sulfanilamide was examined for chemotherapeutic activity and was found to be just as effective as was Prontosil in protecting mice and rabbits against experimental streptococcal infections.

The discovery of the action of sulfanilamide gave to the medical profession a compound simpler and cheaper than the Prontosils and one not subject to patent control. Sulfanilamide is a colorless substance; the Prontosils are red dyes. It is quite likely that in their previous thinking most workers had associated antibacterial action with staining ability.



Sulfapyridine
2-Sulfanilamidopyridine

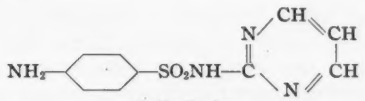
Next to sulfanilamide, sulfapyridine is the compound probably best known to the public. It has been used extensively and successfully against pneumonia. It was mentioned first in 1938, by Whitby, who reported that it was active against experimental pneumococcal infections in mice. It was used clinically almost at once and its use was widespread by the time it was described in the chemical literature. It is active against staphylococcal infections also but the newer sulfathiazole has displaced it largely for this use and also partially for the treatment of pneumonia. Because of irregularities in its absorption by different patients, sulfapyridine cannot be recommended for treating conditions that respond well to sulfanilamide. Furthermore, sulfapyridine is much more expensive. Although the high cost of sulfapyridine may be ascribed in part to patent control, it is unavoidably more expensive to manufacture; α-aminopyridine naturally is more expensive than ammonia. It seems that the toxicity of sulfapyridine is due primarily to the deposition of the more insoluble acetylsulfapyridine in the kidneys. Since individuals vary in the extent to which the drug is acetylated in the body, variations in toxicity are not surprising.



Sulfathiazole
2-Sulfanilamidothiazole

Sulfathiazole is similar to sulfapyridine in effectiveness against pneumonia and in addition is useful against staphylococcal infections. For the latter it seems to be the best drug available. Like sulfapyridine it was used

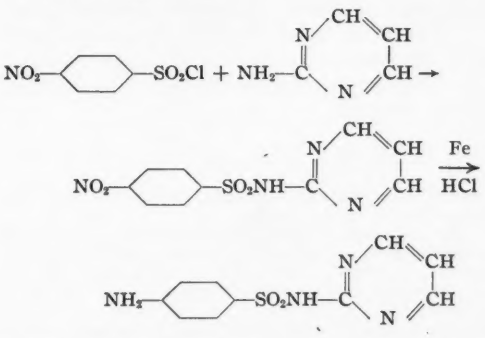
medicinally before it was described in the chemical literature. The description of sulfathiazole actually preceded that of sulfapyridine although the latter came into use first.



Sulfadiazine
2-Sulfanilamidopyrimidine

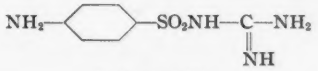
If the precedent established in assigning common names to sulfapyridine and sulfathiazole had been followed, 2-sulfanilamidopyrimidine would have been called sulfapyrimidine. Because this name was so similar to sulfapyridine that the two might have been carelessly mistaken for each other, the name sulfadiazine was chosen by Roblin and co-workers, who first described it. They reported this compound and several other N^1-heterocyclic sulfanilamides in a paper published in 1940. Preliminary mouse tests indicated that the compound was quite active. Later that year, more thorough tests on experimental animals were reported indicating that sulfadiazine was effective against pneumococcal, streptococcal, and staphylococcal infections, and also those due to Friedlander's bacillus B. Furthermore the toxicity tests on monkeys indicated strongly that in the effective dosages sulfadiazine would be less likely to cause unpleasant reactions such as nausea and vomiting, or dangerous effects such as kidney damage. Clinical tests have confirmed these indications and sulfadiazine now has come into general use.

It was made from *p*-nitrobenzenesulfonyl chloride and 2-aminopyrimidine.



This method is expensive because of the cost of making *p*-nitrobenzenesulfonyl chloride and we have no assurance that this is the process being used commercially. The method, however, is convenient for making small quantities of new compounds when the preparation from acetylsulfanilyl chloride does not give results readily. If, as in this case, the compound proves to be valuable, its preparation by the latter method probably is worked out.

Sulfaguanidine is a compound with an absorbing history, indeed. During the course of investigations on heterocyclic derivatives related to sulfapyridine, Roblin and Winnek obtained sulfanilylguanidine in attempts to prepare 5-sulfanilamidotetrazole. This probably was a very lucky accident. They reported that the compound was only slightly active but a more thorough investigation by Marshall and co-workers, who independently synthesized the compound, revealed that it was one of the most active sulfanilamide derivatives.



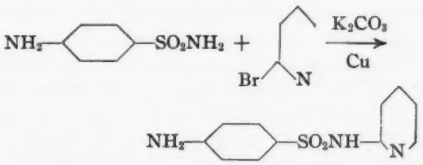
Sulfaguanidine
Sulfanilylguanidine

Though soluble, the compound is poorly absorbed and this makes it less satisfactory for the type of diseases against which sulfonamide drugs are most often used. This apparent weakness is in fact its greatest point of strength. Poor absorption makes it valuable for clearing the bacteria out of the intestines in dysentery or before operations on the lower intestine. The results of trials in such operations have been satisfactory and these operations are common and exceedingly dangerous because of the inevitable risk of infection.

PREPARATION OF COMPOUNDS

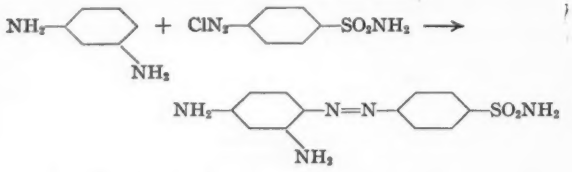
The methods used to prepare most of these compounds are comparatively simple. Most sulfanilamide derivatives for which methods of preparation have been published have been made by slight modifications of Gelmo's method. N^1-Substituted sulfanilamides are made by using the required amine instead of Gelmo's ammonia. They may be made also by treating the amine with *p*-nitrobenzenesulfonyl chloride and then reducing the nitro group to an amino group. *p*-Nitrobenzenesulfonyl chloride seems to react with amines more rapidly and with less formation of by-products than does acetylsulfanilyl chloride. At any rate, it sometimes is more convenient to prepare a new sulfanilamide derivative from the nitro chloride. If a compound made from the nitro chloride happens to be promising enough for extended pharmacological and clinical study, its preparation from the acetamido chloride can be studied later. Once its properties are known, its preparation by the latter method may be somewhat facilitated.

N^1-Substituted sulfanilamides may be made also by direct substitution of sulfanilamide. For example, sulfapyridine has been made from 2-bromopyridine, sulfanilamide, anhydrous potassium carbonate, and



copper powder. The yield was not reported, but the method was extended to the preparation of several related compounds, the yields of which were satisfactory enough to indicate that this method is practical.

Any N^1-substituted sulfanilamide then can be converted to an azo compound of the Prontosil type by diazotization followed by coupling with a phenol or an aromatic amine. Thus Prontosil can be made from diazotized sulfanilamide and *m*-phenylenediamine.



The papers describing new sulfanilamide derivatives often are incomplete in certain respects. New intermediates, particularly N^4-acetylsulfanilamides and *p*-nitrobenzenesulfonamides, frequently are not described although the sulfanilamide derivatives admittedly were made from them. The exact method of synthesis sometimes is not stated.

TESTING FOR ACTIVITY

Groups of compounds, more or less related in structure to compounds known to be active, are synthesized and then tested for curative action on infected animals, usually mice. They cannot be tested satisfactorily on bacterial cultures outside the animal body because there is frequently a tremendous difference between their action *in vitro* and *in vivo*. Domagk found Prontosil to be without effect on bacterial cultures in spite of its high therapeutic activity.

Toxicity tests also must be made. To be valuable as a drug a compound should have a high therapeutic index, which is the ratio between the toxic dose and the therapeutic dose. A compound twice as active therapeutically as sulfanilamide would not be superior if it were four times as toxic.

If a compound appears to be particularly effective in the animal tests, it may be tried clinically; but only after it has proved itself thoroughly in clinical trials is it likely to come into general use. Actually, few prospective drugs get past the animal tests. Many are completely worthless; others are inferior to drugs already in use.

The whole problem of testing the prospective drugs is a complex one and its many ramifications can only be hinted at here. Some are: the use of different methods and schedules of dosage; the difference in susceptibility between different strains of the same bacteria; variation in the response received by using the same compound against the same infection in different species of animals; the difference in blood concentration produced by the same dose of different drugs; differences in the ability of different compounds to penetrate to all parts of the body; the lack of a direct relationship between acute and chronic toxicities; the tendency of compounds to produce in man reactions that are due to hypersensitiveness and idiosyncrasy.

A hint of the complexity of the problem of relative toxicities is given by the fact that for mice sulfathiazole is more toxic than sulfapyridine but for rats and monkeys the order is reversed.

RELATION OF STRUCTURE TO ACTIVITY

Although many interesting relationships have been discovered, it cannot be emphasized too strongly that the study of the relationship between chemical constitution and antibacterial action is essentially an empirical science. The active compounds are discovered by a combination of patient, systematic, empirical study and happy coincidence.

Slight changes in structure often destroy activity but even drastic changes do not always do so. It has been found that the activity of sulfanilamide is destroyed by such minor modifications as the removal of the amino group to the position ortho or meta to the sulfonamide group or the introduction of a carbon atom between the benzene ring and the amino or sulfonamide group. In contrast, activity is retained when the nitro group is substituted for amino. In fact, *p*-nitrobenzenesulfonamide is more active than sulfanilamide but unfortunately also more toxic. Even *p*-nitrobenzoic acid and *p*-nitrotoluene have slight activity. Di-(*p*-aminophenyl)sulfone is highly active. Also, activity has been found in certain compounds of arsenic and phosphorus that are somewhat similar in structure to the active compounds of sulfur.

Just how the sulfonamide drugs work is still an unanswered question in spite of the many theories that have been proposed. They are remarkably effective when given to infected animals but often almost without effect on bacterial cultures *in vitro*. This is undoubtedly one of the primary reasons why little has been deduced about the relationship between chemical structure and therapeutic action. That the mode of action of this new class of drugs should be unknown is not surprising; the mode of action of arsphenamine against syphilis is still unknown more than thirty years after its discovery by Ehrlich.

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Note.—A subject of such importance naturally has received wide publicity. Unfortunately, the newspapers and popular magazines have disseminated much misinformation. Prontosil and sulfanilamide have been used synonymously; sulfanilamide has been called a red dye, Domagk has been credited with the *discovery* of Prontosil and even of sulfanilamide! The student wishing to read on this subject must steer a clear course to avoid on the one hand the majority of popular articles, which will mislead him because of their errors, and on the other hand the majority of scientific papers, which will only confuse him with their mass of detail and puzzle him because they are written on the assumption that the reader is thoroughly familiar with the background of the subject.

The interesting article in Fortune (*9*) would be a good place to start. This might be followed by the historical chapter in Long and Bliss (*6*, Chapter 1), Marshall's discussion (*8*), and finally by Northey's review (*7*). The student's individual interest then could guide him; if he reads French and German, the first hand accounts (*1*, *2*, *3*) of the basic discoveries should interest him. The list might be extended almost indefinitely but need not be, as extensive bibliographies are found in some of the references listed (*5*, *6*, *7*).

THE REGION OF MAXIMUM BUFFER CAPACITY

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WHEN a weak monobasic acid, such as acetic, is titrated with a strong base, such as sodium hydroxide, there is a point in the titration at which the solution exhibits its greatest buffering capacity. To find this point:

Let HA represent the acid, C its concentration, and Ka its dissociation constant; then

$$HA \rightarrow H^+ + A^- \text{ and } \frac{(H^+)\,(A^-)}{(HA)} = Ka$$

Rearranging gives,

$$\frac{1}{(H^+)} = \frac{1}{Ka} \times \frac{(A^-)}{(HA)} \qquad (1)$$

If we assume that the salt formed during the titration is completely ionized and that the ionization of the acid is comparatively negligible, then, after some of the acid has been titrated, the following relationship holds:

$$(HA) = C - (A^-)$$

Substituting this value in (1) and taking logarithms of each side gives

$$\log \frac{1}{(H^+)} = \log \frac{1}{Ka} + \log (A^-) - \log [C - (A^-)]$$

but by definition, $\text{pH} = \log \frac{1}{(H^+)}$ so that

$$\text{pH} = \log \frac{1}{Ka} + \log (A^-) - \log [C - (A^-)] \qquad (2)$$

This is the approximate equation relating the pH of a solution of a weak acid to its dissociation constant Ka, its concentration C, and the concentration of its salt (A^-), over most of the neutralization range.

The solution will exhibit its greatest buffering capacity when the rate of change in pH with change in (A^-) is least. This occurs when the slope of the curve given by the equation is a minimum. The first differential of the equation is the equation for the slope.

Differentiating with respect to (A^-) gives

$$\frac{d\text{pH}}{d(A^-)} = 0 + \frac{1}{(A^-)} + \frac{1}{C - (A^-)} \qquad (3)$$

The second differential is

$$\frac{d^2\,\text{pH}}{d(A^-)^2} = -\frac{1}{(A^-)^2} + \frac{1}{[C - (A^-)]^2}$$

The slope is a minimum when the second differential is zero or when

$$\frac{1}{(A^-)^2} = \frac{1}{[C - (A^-)]^2}$$

from which

$$(A^-) = {}^1/_2 C$$

Therefore, the solution exhibits its greatest buffering capacity when the acid is half titrated.

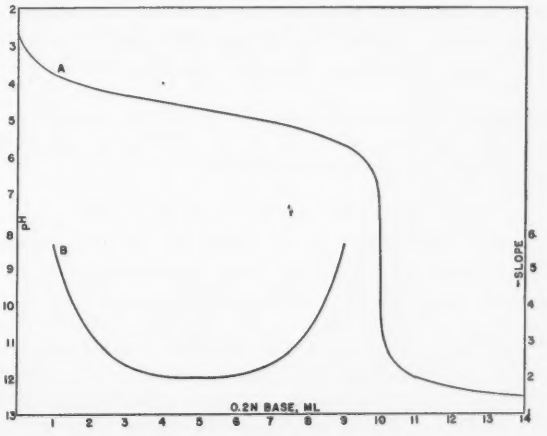

FIGURE 1

Figure 1 (A) shows the changes in pH which occur during the titration of 10 ml. of 0.2 N acetic acid with 0.2 N sodium hydroxide. (B) is a plot of the equation (3) for the slope over the portion where buffer action is significant.

Soap and Glycerol

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SOAP is almost as essential as food, and is closely related in the sense that it is made from many of the same fats which are used for food, after further refining. In the rationing of a country at war soap is usually rationed with food. Any salt of a fatty acid is a soap, but common terminology provides a special meaning, since only the water-soluble salts have detergent properties. The salts of fatty acids with iron, aluminum, and other heavy metals are insoluble in water, distinguished by the term heavy-metal soaps. Some are important in lubricating greases, waterproofing, paint driers, talcum and face powders. Soaps of calcium and magnesium are precipitated from soluble soaps in hard water as the familiar "ring around the bathtub." Soaps formed by reaction of ammonia, triethanolamine, morpholine, and many other amines with stearic or oleic acid are emulsifying agents, stable only in solution. As distinguished from these, ordinary soap consists of the solid sodium salts of fatty acids containing from 8 to 18 carbon atoms. Production of ordinary soap in the United States for household and industrial use exceeds 25 pounds per person annually.

While chemical names will be used here, the soap industry frequently uses trade or industrial terms, such as glycerin instead of glycerol, caustic soda, or soda, for sodium hydroxide, lye or soda lye for sodium hydroxide solution, potash or caustic potash for potassium hydroxide, soda ash for anhydrous sodium carbonate. Likewise soap makers refer to the amount of tallow, coconut oil, or other fat in a soap, although the fat, strictly speaking, is no longer present as such, but has been "saponified" or combined with alkali to form soluble soaps.

Since for every 100 pounds of anhydrous soap nine to ten pounds of glycerol are produced, the soap and glycerol industries are inseparable.

SOAP SOLUTIONS AND THEIR PROPERTIES

All solutions of soap in water are alkaline. However much one may hear about neutral soaps, that is purely a chemical description, meaning that the soap contains no free alkali. Any aqueous solution of a neutral soap has a pH value of 10–10.2, which indicates that it is somewhat more alkaline than any solution of sodium bicarbonate or borax, and somewhat less than that of even dilute solutions of sodium carbonate or trisodium phosphate.

The cleansing power of a soap solution is due to a combination of physical-chemical properties. Because the soap gives an alkaline solution in water it neutralizes acidity normally present in "soil," or dirt which it is intended to remove. This property is enhanced by alkaline "builders" often added. The soap solution thoroughly wets the soil and the surface to which it adheres, thus separating one from the other. The soap solution then generally separates the particles of soil and finally disperses or emulsifies them, so that they remain in suspension and can be rinsed away, without depositing again on the surface being cleaned. The entire problem is a complex one of electrical changes.

When used on the skin, soaps occasionally produce an irritation. This is sometimes popularly attributed to free alkali in the soap. Unless due to excessive exposure to soap and water it is most apt to be either an allergic reaction to coconut oil soap or an irritation caused by the perfume oil present. It follows that such a reaction is as likely to result from high-quality and expensive soaps as from low-priced large-volume bars.

CALCIUM AND MAGNESIUM REMOVAL

The objectionable formation of insoluble precipitates of calcium and magnesium soaps in hard water was a problem which was partially solved in about 1936. If calcium or magnesium soap is added to a solution of one of the complex phosphates it dissolves and the solution will foam as though it contained sodium soap. In water alone calcium and magnesium soaps do not foam. If the complex phosphate is present in hard water soap does not form a precipitate; if the complex phosphate is absent calcium and magnesium soaps are precipitated.

Complex phosphates having this property are tetrasodium pyrophosphate, sodium hexametaphosphate, sodium tetraphosphate, and sodium tripolyphosphate. Failing any more satisfactory explanation it is believed that the complex phosphate sequesters (removes) the calcium and magnesium by forming a water-soluble complex compound which is but slightly ionized.

This is only a partial solution of the problem, because while such complex phosphates are used as "builders" in soap beads and granules, as yet no satisfactory method of incorporating them in cake soap has been found.

CHEMISTRY OF SOAP MANUFACTURE

The simplest method of manufacturing soap is by neutralization of a fatty acid with an alkali, as follows:

$$\underset{\text{stearic acid}}{C_{17}H_{35}COOH} + \underset{\text{sodium hydroxide}}{NaOH} \rightarrow \underset{\text{sodium stearate}}{C_{17}H_{35}COONa} + \underset{\text{water}}{H_2O} \quad (1)$$

In this equation and in others that follow stearic acid is used to represent the mixtures of fatty acids always used commercially. Although this process appears simple it is never applied commercially on a large scale because of high cost. The corresponding reaction with sodium carbonate is used to a limited extent:

$$2C_{17}H_{35}COOH + Na_2CO_3 \rightarrow 2C_{17}H_{35}COONa + CO_2 + H_2O \quad (2)$$

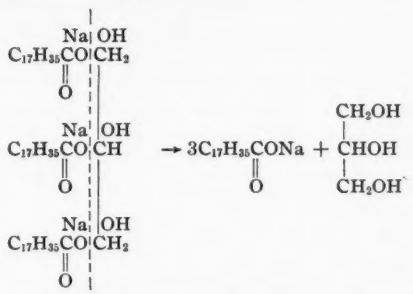
stearic acid — sodium carbonate — sodium stearate — carbon dioxide — water

The principal method of production of soap is by the reaction of an aqueous solution of caustic soda with the commercial saponifiable oils, which are complex esters of one molecule of glycerol with three molecules of fatty acid, as, for example, in glyceryl stearate. This reaction can be represented in an equation as

$$(C_{17}H_{35}COO)_3C_3H_5 + 3NaOH \rightarrow 3C_{17}H_{35}COONa + C_3H_5(OH)_3 \quad (3)$$

glyceryl stearate — sodium hydroxide — sodium stearate — glycerol

or diagrammatically as



$$\rightarrow 3C_{17}H_{35}CONa + CHOH(CH_2OH)_2 \quad (4)$$

Purely as a method of explanation one may assume that the glyceryl stearate reacts with water to form stearic acid and glycerol and that the stearic acid then reacts with alkali to form the soap, but with the understanding that this is only a simplification for purposes of explanation.

$$(C_{17}H_{35}COO)_3C_3H_5 + 3HOH \rightarrow 3C_{17}H_{35}COOH + C_3H_5(OH)_3 \quad (5)$$

$$3C_{17}H_{35}COOH + 3NaOH \rightarrow 3C_{17}H_{35}COONa + 3HOH \quad (6)$$

Addition of (5) and (6) gives (3). Thus it follows that, as mentioned in the introduction, glycerol production is an integral part of soap manufacture. That is true even if fatty acids are used for the actual soap manufacture, as glycerol is produced at the same time as the fatty acids, and then the latter are separately made into soap.

SOAP STOCK

The fatty materials used to produce soap are known as the soap stock. This fatty material may be a solid at ordinary temperatures such as tallow, a liquid such as olive oil, or either a solid or liquid if the melting point is close to room temperature, as is coconut oil, the melting point of which is about 20°C. For convenience they are called fats or oils interchangeably.

Any saponifiable oil will produce a soap of some sort. Only the oils which consist of esters of fatty acids with glycerol fall in this class. A few of these are impractical because the soap is not of the desired quality, many others because of cost. While experimental lots of acids closely allied to the fatty acids have been produced from paraffin or petroleum oils and neutralized to produce soap-like products, there is as yet no indication that these will become commercially practical.

Soap stocks are received in tank cars or casks, melted, separated from any water present, and run into storage tanks provided with closed heating coils. This is necessary to provide for remelting when the stock is to be drawn off to the soap kettle.

The most widely used soap stock is tallow, which is the white to cream-colored solid fat rendered from the fatty tissue of cattle, horses, and sheep. The grades from these different sources vary but little in chemical composition. There are edible grades which seldom find their way into the soap kettle and lower grades which usually do. The principal ingredients are the glycerides of stearic acid, palmitic acid ($C_{15}H_{31}COOH$), and oleic acid ($C_{17}H_{33}COOH$), roughly amounting to two-thirds of the first two and one-third of the latter. Tallow produces a firm soap of high quality which dissolves rather slowly and is preferably used either in blends with other soap stocks or for soap to be used only in hot water. Closely related soap stocks are "white grease," an inedible oil from the kidneys and back of hogs, and "yellow grease" from other parts of the hog. These are used for blending in place of tallow because of their similarity in chemical composition. Lower grades of greases used in lower quality soaps include house grease, garbage grease, and extraction grease derived from refuse, which are either purified to an adequate degree to be suitable for soap making or used for production of fatty acids by the Twitchell process. Fatty acids so produced may then be used in soap manufacture.

Depending on the market price and the availability, whale oil is at times used in considerable amounts as soap stock. The oil is rendered from the blubber or protective layer of fat which lies under the skin of the whale. It has a fishy odor and requires hydrogenation and deodorizing before use. This process consists of passing hydrogen through the heated oil in which nickel or some other catalyst is suspended. Hydrogen adds on at the double or triple bonds of the unsaturated glycerides. The reaction may be controlled for partial or complete conversion to glyceryl stearate. Whale oil when so hydrogenated is a substantially odorless solid fat, replacing part of the tallow in a soap stock. Other fish oils are similarly treated to a limited extent. Any liquid oil could be hydrogenated if price permitted.

Coconut oil is an important soap stock imported from the Philippine Islands. The fruit of the coconut palm is opened and the meat removed and dried. This is the copra of commerce, which contains over 50 per cent of oil. From it the coconut oil is pressed out. This crude coconut oil may be refined for edible purposes or the crude grade may be used as soap stock. Refined grades are often used in the production of paste potassium soaps and liquid soaps.

Coconut oil is composed mainly of glycerides of saturated acids of lower molecular weight than those present

in the usual commercial fats, the major ones being lauric and myristic glycerides. It saponifies readily to produce a firm soap. The soap lathers readily and coconut oil is therefore almost always present in blends of stocks for household soaps.

Palm kernel oil, derived from the kernel of the West African or Sumatran palm nut, is similar in composition and properties to coconut oil, and is not to be confused with palm oil, which is of different composition and derived from the outer pulp which surrounds the kernel. Babassu oil and cohune oil are similar but supplies of them are very limited.

Palm oil is a yellow to reddish brown soft fat composed of the glycerides of palmitic and, to a lesser extent, stearic and oleic acids. Commercially it is usually somewhat rancid, which means that it contains free acid, even up to 20 per cent. Before use it is usually bleached, either with sodium bichromate and hydrochloric acid or by air. Palm oil is easily saponified and gives a hard soap. Therefore it is a major soap fat which may be blended with tallow in a soap stock.

Refined grades of cottonseed, sesame, linseed, peanut, and soya bean oils are too expensive and not suitable for manufacture of toilet soaps. Every one of them is used to some extent in the manufacture of paste potassium soaps and liquid soaps. For this purpose corn oil tends to predominate. U.S.P. potassium soap for surgical use must be made with linseed oil.

In the process of refining, fats and oils are generally melted, sufficient alkali added to neutralize the free acidity, and after further processing "foots" are settled out. These foots are a liquid, often containing only about 50 per cent of fat or oil, but are sold at a low enough price to be used in low grade soaps. After removing the foots the fats or oils are sometimes further bleached by adding fuller's earth or activated carbon.

Castor oil is relatively expensive and gives a soap inferior in detergent properties. It is sometimes used in making liquid shampoo soaps because of its high solubility and the assistance it gives in keeping the shampoo clear.

Because of taxes on edible olive oil, a denatured grade containing oil of rosemary is imported for soap manufacture. Even then it is an expensive stock used only in olive castile and olive shampoos, to give a soap which lathers readily in cool water. While at one time castile soap was synonymous with olive oil soap that has not been the case for several decades. Olive oil foots are a better quality of commercial soap stock than other foots. Used in toilet soaps, they impart a green color to the soap but not all green soap is colored by olive oil foots.

Gum rosin or wood rosin, while not fats, nor even derivatives of fatty acids, are used to a limited extent as soap stock. They consist largely of abietic acid, a complex acid, or the anhydride of abietic acid, and variable amounts of impurities according to the quality. Being largely a free acid, rosin can be saponified with excess of sodium carbonate—sodium hydroxide is not required. Rosin in soaps causes them to lather freely; too large an amount renders them sticky. It is commonly used in yellow-bar laundry soaps—rarely in white toilet soaps, and then only in small amounts.

Any type of soap stock may be rancid, as indicated by an unpleasant odor, and shown chemically by the presence of aldehydes. It may be high in fatty acid and therefore low in fatty glycerides. The two conditions are commonly but not necessarily associated. If a soap stock is to be stored for some time, and the development of rancidity is to be avoided, air, light, moisture, and heavy metals must be absent.

The soap stock must be carefully selected according to the quality of soap to be made, as it constitutes on the average about 90 per cent of the raw material cost. If it contains several per cent of fatty acid or is rancid, it is a low grade soap stock. A high content of unsaponifiable matter may impart undesirably slow solubility. Unpleasant odors in the soap stock often carry over into the finished soap unless the soap stock is separately deodorized, which is expensive. Other impurities and water in the soap stock are purely waste. The color of the soap stock is important as affecting the color of the finished product, white soaps being at a premium.

Unsaturated oils such as corn or olive, which are available as foots, tend to give softer soaps; saturated oils or fats such as tallow or coconut oil give harder soaps. Sodium soaps are harder and less easily soluble in water than potassium soaps of the same oils. But a hard bar of soap may often contain some potassium soap. Commercial soft soap is obtained either by supplying a high water content, using an unsaturated stock, or using potassium hydroxide for saponification.

OTHER RAW MATERIALS

The alkalies can be passed over briefly. Sodium hydroxide and potassium hydroxide are products of electrolysis of the corresponding chlorides and will normally be 98 to 99 per cent pure. Alternatively sodium hydroxide is produced by reaction of lime and sodium carbonate solution, a process called causticizing soda ash. For use in white soaps the alkalies *must* be iron-free, and for other soaps they *should* be, to avoid development of rancidity in the finished soap. Sodium carbonate used for saponifying fatty acids is commercially more than 99 per cent pure.

The principal inorganic "builders" added to increase alkalinity are, in order of amounts used, sodium silicate or water glass, tetrasodium pyrophosphate, sodium metasilicate, sodium carbonate, and trisodium phosphate. Such builders in proper amounts decrease the net cost of the soap without proportionately decreasing its efficiency and therefore represent an economy for the purchaser.

Many soaps contain a fraction of a per cent of sodium silicate to prevent development of rancidity, an amount insufficient to serve as a builder. In others small

amounts of sodium sulfite or sodium thiosulfate serve the same purpose.

No white soaps and few bar soaps of any type are marketed without an added perfume. In many cases these are added so judiciously that the popular impression is that the odor is one natural to soap. For the important white soaps the perfume is usually a blend in which citronella predominates. Toilet soaps usually have flower-type odors added.

TYPICAL SOAP COMPOSITIONS

A bar soap contains from about 10 to over 40 per cent of water. Soap without added builder as it comes from the soap kettle contains 30 to 33 per cent of water, which may be reduced by further processing. Other non-soap ingredients present in addition to builders are usually a fraction of a per cent of salt, a fraction of a per cent of unsaponified fat, from 0.05 to 0.1 per cent of free alkali, and incidental impurities in very minor amounts.

Chip soap used for commercial laundering usually contains 88 to 92 per cent of soap made from straight tallow stock. Builder is separately added by the laundry.

White household soap for general use is usually made from tallow stock with an addition of 10 to 35 per cent of coconut oil. The tallow may be replaced in part by greases or bleached palm oil. This usually floats due to the presence of air beaten in during "crutching." It contains about 30 per cent of moisture.

Milled toilet soap, the aristocrat of the industry, contains only about 11 to 13 per cent of moisture and no builder. A fraction of a per cent of zinc oxide or titanium dioxide is added as a white pigment to improve the whiteness of some of these soaps, having no other effect on their properties. The stock is usually tallow and coconut oil, but other good quality stock such as palm oil and the better greases may replace part of the tallow. Some softer types contain substantial amounts of soaps of the liquid oils such as foots of corn, cottonseed, or olive oil.

Household chip soaps are of the same composition as hard milled soaps, but in their flake form are a little lower in moisture content. Household bead or granule soaps normally contain about 50 to 60 per cent of hard soaps, 10 to 20 per cent of moisture, and the balance of builder. A representative composition of such a builder would be 15 per cent of tetrasodium pyrophosphate, 7 per cent sodium metasilicate, and 8 per cent sodium carbonate.

White laundry bar soap is made from the lowest grade white stock possible, such as the cheaper greases, with some coconut oil and as much as 35 to 40 per cent of sodium silicate. In yellow laundry soap the cheaper grades of liquid oil foots, such as cottonseed oil foots, can be used. Rosin replaces the coconut oil and may amount to 25 to 30 per cent of the soap stock, and the amount of sodium silicate added is only about 20 per cent. Rosin and liquid oils inherently produce a softer bar.

Such laundry soaps are a steadily declining part of the market, as the tendency is to go to all-purpose soaps—white floating soaps which do not contain builder and are suitable for toilet, household, and laundry purposes. Another part of the market for laundry soaps has been taken by bead or granule soaps, which are "built" to make them more effective in hard water.

Hard-water soaps and salt-water soaps are basically cold-process coconut oil soaps, often with builder added. They are so called because they are more soluble in hard or salt water and in the presence of calcium and magnesium than are ordinary soaps. Some products sold under this name are produced largely from tallow stock.

Castile soaps were originally cold-process soaps made from olive oil, with several per cent of excess oil left in the soap. In modern practice they are often made largely from coconut oil.

Transparent soaps or glycerol soaps are almost obsolete. They are made by dissolving the soap in hot alcohol, with or without addition of glycerol and sugar, and allowing the soap to deposit on evaporation of the alcohol.

Abrasive soaps are either cold-process or half-boiled soaps which have pumice, ground silica, or fine natural sand incorporated. Scouring powders or scouring soaps consist mainly of a coarse abrasive with a minor amount of soap, usually under 10 per cent.

True powdered soaps, such as those introduced into tooth powders, are either high quality soaps dried to less than one per cent moisture and pulverized, or are made by one of the new anhydrous saponification processes. Soaps are also sold containing such substances as cresols, mercury compounds, finely divided sulfur, tar, and other medicating agents.

Shaving cream is potassium soap to which a substantial excess of stearic acid has been added. "Brushless shave" contains stearic acid and fats, with less soap. Benzine soaps or dry-cleaners' soaps are usually oleic or stearic acid dissolved in dry-cleaners' solvent and *half* neutralized by potassium hydroxide. Among the many modifications of these are triethanolamine, ammonia, and morpholine soaps in petroleum solvent. They form a stiff paste rather than a solution, and are not a product of the soap industry proper. Shampoos are usually liquid soaps, although they may be sulfated oils or sulfated alcohols.

There are many specialty soaps such as textile soaps of various kinds, automobile soap, saddle soap, etc. These are other modifications of the basic structure of a fatty acid salt of an alkali metal.

MANUFACTURE IN THE SOAP KETTLE

The steps in the manufacture of soap as carried out in the soap kettle are saponification, graining, and settling. The kettle is usually cylindrical and has either a conical or flat bottom. Internal coils of steam pipes are provided and are conventionally referred to

as closed steam. Steam outlets are separately provided by which steam can be injected into the charge in the kettle, called open steam. The latter permits more rapid heating, with mixing at the same time,

Courtesy of MacNair-Dorland Company

SOAP KETTLES

This view shows the top of large soap kettles which run through two or three floors in most soap factories.

but adds the condensate from the steam to the batch. An outlet provides for withdrawing the bottom layer from the kettle. Some such kettles have a capacity of a half million pounds of soap in a single batch.

In the more modern plants much of the equipment, particularly that for later steps, is of stainless steel, nickel-clad steel, rustless iron, alloys such as Monel metal, or is plated with corrosion-proof metal. This avoids possible contamination of the finished soap by iron, copper, and other metals.

Saponification is carried out in from one to as many as four steps. The variations depend on the type of stock, the quality of soap desired, and the importance of the efficient recovery of glycerol. The simplest form with saponification in a single stage, and a single salting out, will be described.

Part of the charge of oil is pumped into the kettle and open steam is turned on to heat it. Some sodium hydroxide solution is run in, which may be a partially exhausted solution from a previous batch. In the initial stage this solution partially emulsifies the fat and reaction proceeds at a rate dependent largely on the kind of soap stock. More fat and alkali are run in as the reaction proceeds. The operation is largely judged from experience, the soap maker keeping the soap at the necessary degree of liquidity. The saponifying mass should be smooth rather than grainy; this is controlled by the rate of addition of the alkali. The practical test by tasting is commonly used to be sure that some excess alkali is present when the boiling is finished, this being necessary to insure substantially complete reaction of the fat and alkali.

Soap is soluble in hot water but insoluble in salt solution of suitable concentration; a tallow soap will be insoluble in 10 per cent brine, a coconut oil soap in 15 per cent. To remove excess alkali and recover glycerol from the soap, salt is added to "grain" it. If there is an excess of water in the kettle solid salt is used; otherwise the salt is added as a strong solution. When sufficient salt has been added the soap forms coarse soft clots, much like sour milk but larger. Steam is now turned off and the kettle allowed to stand for 4 to 12 hours. The soap rises to the top, the brine containing a fraction of a per cent of free alkali, and 2 to 6 per cent of glycerol settles to the bottom and is withdrawn for recovery of glycerol and salt. This completes the first brine change, what is often called the "killing change."

Saponification of the remaining minor amount of the batch is completed in the "strong change." Often steam is turned on until the batch is hot and water is slowly added until the soap is smooth rather than grained. Strong sodium hydroxide solution is added for a time and thoroughly blended into the soap by boiling the batch, then more is added and again boiled into the batch. This completes the saponification of residual fat without starting the graining. After a few minutes the addition of sodium hydroxide solution is resumed and continued until the soap is grained out. Thus in the strong change the soap is grained out with sodium hydroxide in much the same way that it was previously grained out with sodium chloride.

Steam is then shut off and the sodium hydroxide solution is allowed to settle out as the brine did in the previous change. When withdrawn this contains several per cent of sodium hydroxide and is put aside for use in the first saponification step on a fresh batch. The soap resulting from the strong change will contain around one per cent of free sodium hydroxide.

The last step is the "finishing change." After the strong change and the removal of the sodium hydroxide, the batch is heated up with open steam. Then water is added until this is intermediate between the grained state and the usual smooth condition prior to graining.

Courtesy of MacNair-Dorland Company

SOAP IN FRAMES AFTER COMPLETION OF COOLING

The soap is then in condition for finishing. At this stage a heated steel trowel dipped in the batch will let the soap run off in a thin, almost transparent sheet, while after half a minute large clots will solidify on the trowel.

The steam is then turned off and the soap separates

into two sharply defined layers. This settling will take from a day to a week according to the size of the kettle. The upper layer is finished kettle soap, often referred to as "settled soap," and if of the best quality will contain less than 0.05 per cent of free alkali and only 0.1 to 0.2 per cent of salt. The lower layer or "nigre" is a dark, strongly alkaline soap containing 50 to 60 per cent of water. It is often reworked several times in successive kettles but must eventually be used up in a lower grade soap. Insoluble impurities settle under the nigre.

The settled soap is pumped out through an adjustable pipe to a crutcher or to suitable tanks where it is kept heated until the next operation.

INTRODUCTION OF ROSIN SOAP

When rosin is introduced into soap it is usually done after the saponification of fat, but before the strong change. The rosin may be introduced into the kettle as a separate step in the form of broken-up solid lumps, and saponified in the kettle. In that case the required amount of sodium hydroxide is added to saponify it and the soap is then salted out and settled in the usual way. The brine withdrawn contains no glycerol and goes to waste. This completes the rosin change, introduced before the strong change.

An alternative procedure is to introduce the rosin into a separate kettle and nearly complete its saponification with sodium carbonate. When this is done the rosin soap is salted out in that kettle, settled, and pumped into the main kettle before the strong change. The saponification of the rosin is then completed in the strong change and the rest of the steps are as usual.

CRUTCHING AND FRAMING

A vertical "crutcher" is a mixing tank with an Archimedes screw rotating in the center and is usually provided with both open and closed steam. The finished, settled soap is pumped into it, usually through a screen. Much clean scrap soap is produced at the later stages which can be introduced into the crutcher and melted in with the batch. As an alternative, this scrap soap is remelted separately and added in molten form to the soap in the crutcher. Dirty soap scrap goes back into the kettle with a batch being saponified. Perfumes and builders are added and mixed in by rotating the screw continuously upward. The contents are then ready to drop into frames.

The soap frame is a box mounted on rollers, having removable sides and ends. A frame is usually somewhat over $4\frac{1}{2}' \times 3' \times 1'$. The hot soap is run in and allowed to cool for three to five days. The sides and ends are then removed.

An alternative form of crutcher is horizontal and has a series of short paddles pitched at a sharp angle. It will mix air into the soap unless it is full.

FLOATING SOAPS

Soap has a specific gravity of about 1.05. If the screw of the crutcher is revolved downward it mixes air into the soap. This is frequently supplemented by blowing air in through small pipes located in the bottom of the crutcher, to speed up the operation. This air, present as bubbles, lowers the effective specific gravity of the soap to 0.8–0.9. This aërated soap must be cooled in the crutcher to a point just short of congealing before it is dropped into frames; otherwise too much of the air will escape. Only soap stocks of the better qualities are used for floating soaps. The "framed" floating soap is then finished in the same way as other framed soap.

SLABBING, CUTTING, PRESSING, AND WRAPPING

The block from the frame, weighing over 1000 pounds, is scraped lightly on the sides to remove dirt or rust and then forced through a row of stretched piano

Courtesy of MacNair-Dorland Company

CUTTING AND RACKING SOAP

wires. This first cuts it into slabs the small way of the frame. These slabs are cut in turn into long bars by other wires; the bars are then cut crosswise into the individual cakes of soap which are spaced on trays for handling.

These trays may be placed in a dry room but are frequently passed through heated tunnels to dehydrate the surface layer of the soap in part. The cakes are then pressed in stainless steel dies, to brand the bar, and wrapped, usually in a double wrapper of which the inner layer is waterproof and alkali-resistant.

HALF-BOILED AND COLD-PROCESS SOAPS

If the soap stock is free from dirt and other material which would be undesirable in the finished cake, the theoretical amount of alkali for saponification can be added with sufficient water to give the finished composition. This batch is allowed to react in the crutcher with only sufficient heat to produce the reaction, then perfumed and framed or otherwise treated in the same way as kettle soap. Since the soap is not salted out the glycerol produced is left in the soap. This is known as half-boiled soap.

And also, without heating, the theoretical amounts of melted fat, alkali, and water can be mixed by hand or mechanically until homogeneous. When saponification has proceeded so far that the batch is thick, it can

then be allowed to continue by itself. The initial stages may be carried out in a crutcher or, in the cruder plants, directly in a soap frame. This is cold-process soap. The usual practice is to use slightly less than the theoretical amount of alkali in order to leave the soap with a small amount of unsaponified fat. Such soaps are called superfatted soaps. Scrap soap cannot be introduced in this process.

Superficially, the half-boiled and cold processes seem advantageous because they are simple. The higher cost of the quality of fats required and the lack of recovery of glycerol more than offset the simpler method of manufacture, so that neither half-boiled nor cold-process soaps are really important in the market. The half-boiled process is used in production of paste potassium soaps to be sold as such or made into liquid soaps. The cold process is used in manufacture of castile-type soaps.

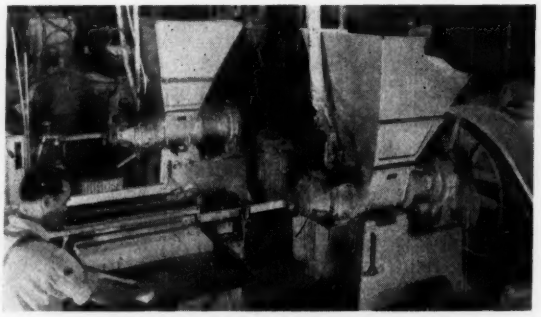
MILLED SOAP

The bar of framed soap containing 28 to 30 per cent of water is usually soft enough to be indented by vigorous pressure of the thumb. For fine toilet soap a harder cake of smoother texture is desired. To obtain this, settled soap made from the best quality soap stock is discharged as a thin layer from the storage tank onto chilled rolls. These cool it as a thin film during passage through a series of three or four rolls. Cutting units mark it as strips which are removed by a fixed knife against which the last roll turns. The strips of soap, still containing around 30 per cent of moisture, chip off and drop to a continuous belt which passes through a drying tunnel. This reduces the moisture content to 12 to 15 per cent. These chips are then

Courtesy of MacNair-Dorland Company

MILLING OF TOILET SOAP

mixed with perfume and other minor ingredients such as pigment and fed to mills which work the soap on the rolls at room temperature. This milling operation warms the soap, makes it smoother and also more transparent, unless pigment has been added. While still warm these chips are fed to a continuous screw machine known as a "plodder" which squeezes them into a mass and forces them through a plate with holes, usually about one to three mm. in diameter. The



Courtesy of MacNair-Dorland Company

PLODDING TOILET SOAP

Soap is shown extruding from the plodder in an endless bar and being cut into blank cakes which are then pressed into finished form. The plodder takes the soap from the soap mill and forms it into a solid, compact mass.

plodder is water-jacketed to take up the heat produced in squeezing the soap chips. The soap is finally forced through the nose of the plodder, which delivers a continuous bar of the size of the finished cakes. The nose of the plodder is heated in order to give a smoother, more glossy surface to the bar. Suitable lengths for cakes are cut from this bar with piano-wire cutters, stamped to impress the brand, and wrapped as the finished soap. It is not necessary to allow milled soap to dry before pressing as was described for framed soap.

SOAP FLAKES, BEADS, AND POWDERS

For convenience the flakes from the chilled roll and drying tunnel are often packaged as a high grade soap which dissolves more readily than cake soap. This is a quality product. By passing the flakes through a milling operation, a somewhat lower moisture content is obtained; the chips are polished and appear more transparent. Very thin chips are obtained by this process.

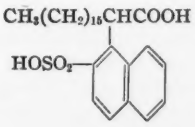
Beads or globules of soap are obtained by an entirely different method. The molten settled soap is blended in a crutcher with suitable builders, usually to the extent of 20 to 30 per cent of the total. In modern practice about half of the builder is tetrasodium pyrophosphate so that the soap will not precipitate calcium and magnesium soaps in hard-water districts. The finished batch is then sprayed into heated air in a tower under vacuum, which vaporizes some of the moisture and gives hollow beads. Another process is to spray the hot soap into very hot air to cause it to dry to a solid as the particles fall.

Soap powders, an entirely different product, are low in soap content. Soaps for this purpose are made from the lowest qualities of soap stock. To a batch of kettle soap containing much excess water, anhydrous

sodium carbonate is added. The final soap content rarely exceeds 24 per cent, and is often around 15 per cent. If less than this, the substance is not properly a "soap powder." The composition in the kettle or crutcher is the same as that of the finished product on congealing. In the most modern plants the material is sprayed into a tower at atmospheric temperature and pressure. The sodium carbonate crystallizes as sal soda, $Na_2CO_3 \cdot 10H_2O$, carrying more or less soap according to the composition. This is in finished form ready for packing. Other plants deliver the composition to chilled steel rolls where it congeals and is subsequently ground and packaged. In the smallest plants the batch is dumped on a concrete floor to congeal, after which it is ground and packaged. Soap powder as a trade term should not be confused with *powdered soap*. The latter term means a pure soap, dried ordinarily to less than one per cent of moisture and ground to a very fine powder.

FATTY ACID MANUFACTURE

Every student of chemistry knows that if fatty glycerides are saponified with sodium hydroxide to soap and then acidified with mineral acid, the free fatty acids corresponding to the soaps are liberated. Practically, that is not the method by which fatty acids are obtained. Fatty glycerides may also be heated in an autoclave with dilute sulfuric acid to react slowly and incompletely with water, according to equation (5). When this process is hastened by a catalyst it is commercially practical—the Twitchell process. The catalytic reagent is prepared by heating naphthalene, oleic acid, and sulfuric acid to produce 2-(β-sulfonaphthyl) stearic acid:



More active reagents have been developed but with structures not well established.

The process permits the use of low grade fats such as very poor foots of the liquid oils, garbage grease, and other dark greases. Such low grade fats are first boiled with open steam and washed with one per cent sulfuric acid to remove as much as possible of the impurities which may act as negative catalysts or poison the reagent.

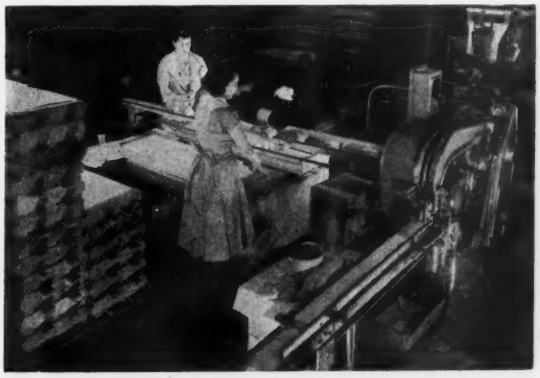
The washed fat is usually placed in a wooden tank, filling it a little more than half full. Then water to about half the weight of the fat, 0.75 per cent of the catalyst, and about one per cent of sulfuric acid are added. The batch is heated with open steam for about 24 hours, the amount of steam being just sufficient to blanket the surface and prevent contact of air with the batch, as air will darken the acids produced. The reaction is 65 to 85 per cent complete at this stage. Condensation of open steam in the batch produces an acid layer underneath, which should contain about 15 per cent of glycerol. This is drawn off and sent to the glycerol plant for treatment. Most of the catalytic reagent remains in the fatty layer.

To complete the treatment, about 25 per cent of water, based on the fatty layer, about 0.5 per cent of sulfuric acid, and about 0.25 per cent more of Twitchell reagent are added. Boiling with open steam is resumed for 16 to 20 hours, in which time hydrolysis will be over 95 per cent complete. The aqueous layer is withdrawn for glycerol recovery and the fatty layer is steam distilled *in vacuo*. By this process colorless or nearly colorless fatty acids are produced which may be sold as such or converted into soaps by neutralization with sodium carbonate as in the continuous processes.

CONTINUOUS PROCESSES

The soap-making processes described are batch processes. From an engineering standpoint continuous processes would be preferred—are usually more economical. Several have been developed.

In one of these, streams of high quality fatty acids, sodium carbonate solution for neutralization, and any builder desired are pumped into a continuous screw type of mixer. Reaction under vigorous agitation is complete in a few seconds and molten soap is discharged at the other end. It may, if desired, have the same composition as finished kettle soap, and can be formed into cakes, beads, or chips.



Courtesy of MacNair-Dorland Company

PRESSING TOILET SOAP

In another process, a stream of fat and a stream of alkali solution are mixed and sprayed into a vacuum. The temperature is sufficiently high so that all moisture and glycerol are withdrawn as vapor. The soap drops to the bottom of the vacuum chamber as anhydrous soap which may be sold as such or further processed.

Of significance in these processes is the fact that a chemical equivalent of sodium carbonate costs about half as much as one of sodium hydroxide.

ALLIED PRODUCTS

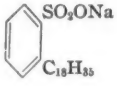
Many products which are not soap nevertheless have similar properties. Sulfated castor oil, incorrectly known as "sulfonated castor oil," is one such, used in shampoos and in dyeing. Sulfation of alcohols of high molecular weight produces a product which is very similar in structure to soap. The reaction is

$$C_{18}H_{35}OH + H_2SO_4 \rightarrow C_{18}H_{35}OSO_2OH$$
$$C_{18}H_{35}OSO_2OH + NaOH \rightarrow C_{18}H_{35}OSO_2ONa$$
sodium octadecyl sulfate

Compare this with soap:

$C_{17}H_{33}COONa$
sodium oleate

These alkyl sulfuric esters are used in the textile industry as wetting agents in neutral and acid solutions, and in the household to replace soap in very hard water. As other salts than those of sodium they are applied as shampoos, as tooth cleaners, and for many other purposes. Another product of the type consists of an alkylaryl sodium sulfonate. A typical example is the following:



These are produced in such quantities as to promise to compete in price with soap, since the raw materials are available in practically unlimited amounts. Blended with suitable builders they can be made into solid bars, but unlike bar soap these tend to disintegrate in water. Their uses are as soap substitutes for many industrial and household purposes. These and a few less important types already represent a large tonnage which is expected to increase but will hardly approach that of soap.

GLYCEROL

This is a by-product of soap manufacture. The glycerol liquors from the soap kettle contain salt, a small amount of soap, free alkali, and 8 to 10 per cent glycerol. When this is neutralized with sulfuric acid and concentrated *in vacuo* to about 50 per cent glycerol in a multiple effect evaporator, the salt drops out of the boiling solution into a salt box and is used over again in the soap kettle. The crude glycerol is filtered and further concentrated to about 85 per cent.

That grade has a market as "saponification crude glycerol," or is refined by steam distillation *in vacuo* to over 99 per cent purity as dynamite glycerol, or to over 95 per cent purity, free from minor discoloring matter, as U.S.P. or C.P. glycerol.

ON THE SWEETNESS OF FAT

THERE is today a gradual trend toward industrial control over rancidity. Rancidity is the generic term for any developed unpleasantness from a fat or oil. In foods such as lard rancidity may pertain either to odor or taste. In fatty non-foods rancidity usually refers to odor alone. Oxidation is the common source of odor deterioration, but some paint oils oxidize readily, and in doing so improve in odor, for oxidation does not necessarily produce bad odors. While strong light may speed up oxidation and produce rancidity in such substances as soybean oil, other causes of rancidity include enzyme action such as that producing strong butter by the release of amines giving a fishy flavor, low bacterial count, metallic contamination in butter, and the enzyme action causing wheat germ to turn bitter.

Any rancidity due to oxidation by the air takes place sooner and faster as the storage temperature increases. It may be initiated by exposure to light. The presence of even minute traces of copper, iron, or a few other metals, greatly accelerates the onset and speed of oxidative rancidity. Moisture generally speeds the rate of oxidation, but in the special case of cornflakes may retard it. In general, any rancidity is latent as long as some protective factor is active, and then develops at a relatively rapid rate. The useful life of a fat ends with the termination of the "induction period," after which deterioration may develop with runaway speed. Control over fat quality consists preferably in conserving any naturally occurring rancidity-retarding influences, and in protecting the fat from outside unfavorable conditions. Sometimes it is permissible to add an antioxidant.

Spoilage of fats, in the final analysis, has to be determined organoleptically, *i. e.*, by taste and by smell. Since this personal testing varies with the skill and experience of the operator and is limited by many factors, effort has been made to find impersonal chemical and physical aids or partial substitutes. Several chemical tests, such as the accelerated peroxide technic, are of value in detecting types of rancidity, and numerous machines have been devised in which oils are measured for their rate of oxygen absorption against time and temperature. In comparing samples of the same oil, the oxygen-absorption rate is usually found to bear some relationship to the tendency to rancidity.

Most oils, especially vegetable oils, are associated with natural antioxidants. The oils are protected so long as the antioxidant is being produced, or commercially, until it is all used up. These "inhibitors" probably vary greatly in different plants. A sizable business has grown up around the extraction of "inhibitors" from plants particularly rich in them and around their concentration for use in fatty compositions. For non-food uses, fats may be preserved with commercial antioxidants of a considerable variety. By keeping fats away from the known unfavorable influences other than the oxygen of the air, such as metallic contamination and exposure to light and heat, they can usually be well protected.

—From the *Industrial Bulletin* of Arthur D. Little, Inc.

Magnetism and Molecular Structure

P. W. SELWOOD *Northwestern University, Evanston, Illinois*

IF A substance is placed in a magnetic field whose intensity may be represented by a certain number of lines per square centimeter, then the number of lines within the substance may be either less or greater than the number in the surrounding space. In the first case the substance is called *diamagnetic*, in the second *paramagnetic*. There is also the case of *ferromagnetism* in which the number of lines is increased a million fold or more. But ferromagnetism, although of great technological importance, is nevertheless comparatively rare in nature, occurring in only a few elements, alloys, and compounds. Paramagnetism is fairly common in nature, while diamagnetism is a universal property of matter. All substances, even though paramagnetic, have at least an underlying diamagnetism that must be corrected for in precise determination of the permanent magnetic moment. That is, the substance may be both diamagnetic and also paramagnetic, but generally whenever paramagnetism is present it is so much larger that it hides the diamagnetism.

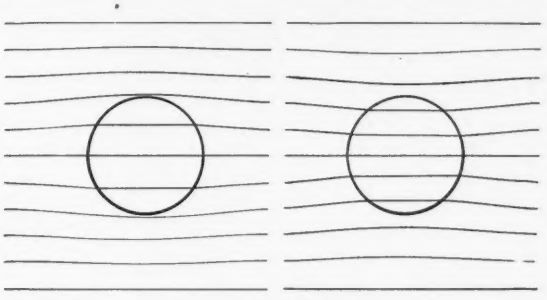


FIGURE 1

Diamagnetic bodies (*left*) are less permeable than a vacuum to magnetic lines of force. Paramagnetic bodies are more permeable than a vacuum.

If the initial intensity of the magnetic field is H, then the intensity within the substance is given by

$$B = H + 4\pi I$$

The quantity I divided by H is equal to the magnetic susceptibility per unit volume. Division of this quantity by the density will give χ, the magnetic susceptibility per unit mass.

The magnetic susceptibility of diamagnetic substances is independent of the temperature, while that of paramagnetic substances may often be represented by the expression

$$\chi = C/T$$

where C is the "Curie" constant, and T the absolute temperature. Ferromagnetism depends not only on the temperature, but also in a complicated way on the strength of magnetic field used in the measurements.

Ferromagnetism has probably been known since prehistoric times, but para- and diamagnetism were first discovered by Michael Faraday not much over one hundred years ago. Faraday's work was greatly extended by Pierre Curie and by Pascal about forty years ago, but all their careful researches contributed little to our knowledge of molecular structure. It remained for Professor G. N. Lewis, at the University of California, to point out the intimate relationship between magnetism and chemical valence. During the past twenty years magnetism has slowly become an accepted tool for molecular structure studies. At the present time there is scarcely a chemical journal which does not contain one or more articles on magnetochemistry. On September 10, 1941, the American Chemical Society conducted, at Atlantic City, the first symposium ever held in this country on "Magnetism and Molecular Structure."

The method of Gouy is most frequently used for magnetic susceptibility measurements. This method, shown diagrammatically in Figure 2, uses a large electromagnet between the pole-pieces of which the sample

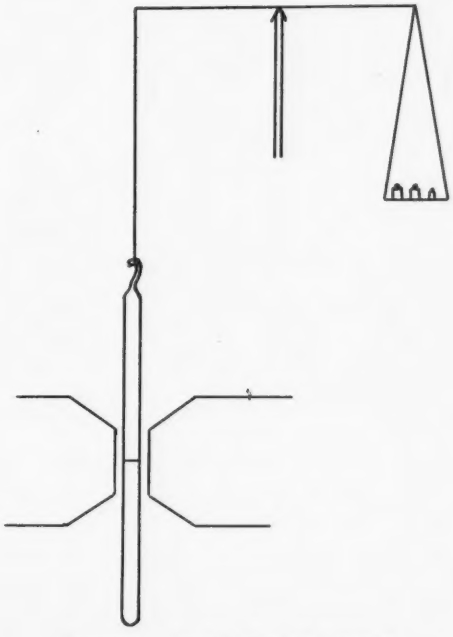


FIGURE 2.—GOUY MAGNETIC BALANCE

under investigation is suspended. One end of the sample is directly between the pole-pieces where the magnetic field is a maximum, the other end extends into a region of relatively low magnetic field. The sample, which may be contained in a glass tube, is suspended

from a balance. On application of the magnetic field the sample will, if diamagnetic, appear to lose in weight. If the sample is paramagnetic it will appear to gain in weight. The force, f, acting on the sample is given by the expression

$$f = \frac{1}{2}(\kappa_1 - \kappa_2)(H_1^2 - H_2^2)A = g\Delta w$$

where κ_1 is the magnetic susceptibility per unit volume of the sample, κ_2 is the susceptibility of the surrounding atmosphere, H_1 is the field strength at its greatest intensity between the pole-pieces, H_2 is the field strength at the upper end of the sample, A is the cross-sectional area of the sample, g is the gravitational constant, and Δw is the apparent change in weight on application of the field.

Water, the susceptibility of which is -0.720×10^{-6}, is often used to calibrate the apparatus.

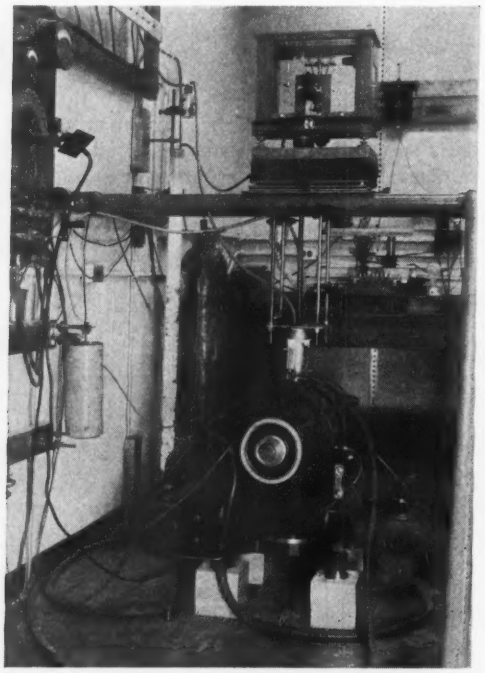


FIGURE 3.—GOUY MAGNETIC BALANCE

Figure 3 is a photograph of a magnetic susceptibility apparatus in use in the author's laboratory. In this apparatus there are several refinements such as use of a micro-balance to measure Δw, thermostating devices by which the temperature may be measured and controlled to at least 0.01 degree, and provision for changing the temperature from $-190°$ to 100°C. There is also a device for maintaining the constancy of the magnetic field. This apparatus is sensitive to about $\pm 0.0001 \times 10^{-6}$ units of magnetic susceptibility and was used in some of the experiments on organic free radicals to be described later. The cost of the apparatus was about $4000.

The Gouy method is applicable to solids, liquids, and in certain cases to gases. It may be used over a wide range of temperature and of field strength. A field strength of 13,000 oersteds is frequently used in the apparatus described above. For handling dilute solutions a differential method is used. In this case the sample tube, made of carefully selected glass, has two ends separated by a glass partition as shown in Figure 4.

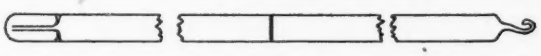


FIGURE 4.—SAMPLE TUBE USED IN THE GOUY MAGNETIC BALANCE

The solution under investigation is placed in the upper part of the tube while the pure solvent is placed in the lower part. The magnetic field is applied in the region of the partition. This sample tube must be supplied with a reservoir for expansion and contraction of the solvent so that the temperature may be changed without either breaking the tube or allowing a bubble of vapor to form at the partition. In the tube shown, solvent completely fills the lower half of the tube proper and half fills the reservoir. Then as the solvent warms up it expands through a little capillary tube into the reservoir, or if the solvent contracts it sucks up more solvent from the reservoir without formation of a bubble at the partition.

Another method which is often used for measuring magnetic susceptibilities is that of Quincke. This is shown diagrammatically in Figure 5. The method is applicable only to liquids, or with certain refinements to gases. In this method the sample is contained in a capillary tube placed between the pole-pieces of the magnet. The field strength is often about 30,000 oersteds. On application of the field the level of the meniscus of the sample will fall if the sample is diamagnetic, or rise if it is paramagnetic. The rise or fall may

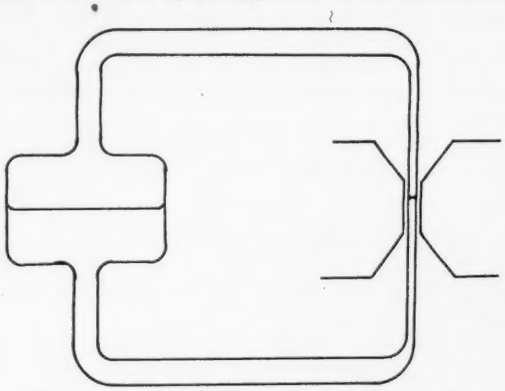


FIGURE 5.—QUINCKE MAGNETIC BALANCE

be observed directly with a micrometer microscope or may be counterbalanced by a change of gas pressure over the meniscus. Sometimes a reservoir connected to the capillary is raised or lowered on a traveling stage so as to counterbalance the movement of the meniscus.

This method does not lend itself so readily to change of temperature, and as stated, it is useful only for liquids. It possesses some advantages such as ease of handling and it may probably be made as accurate as the Gouy method.

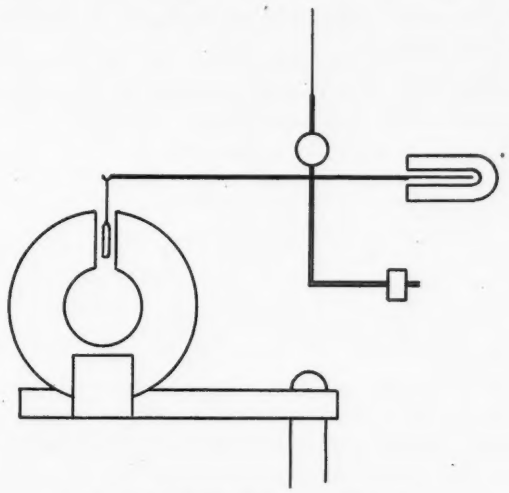


FIGURE 6.—CURIE-CHÉNEVEAU BALANCE

Among the several other methods available for measurement of magnetic susceptibility, the only one necessary to mention is the Curie-Chéneveau balance. This balance is shown diagrammatically in Figure 6 and in a photograph in Figure 7. The balance consists of a torsion arm suspended by a fine wire. One end of the torsion arm supports the sample which is free to move between the poles of a small permanent magnet. The

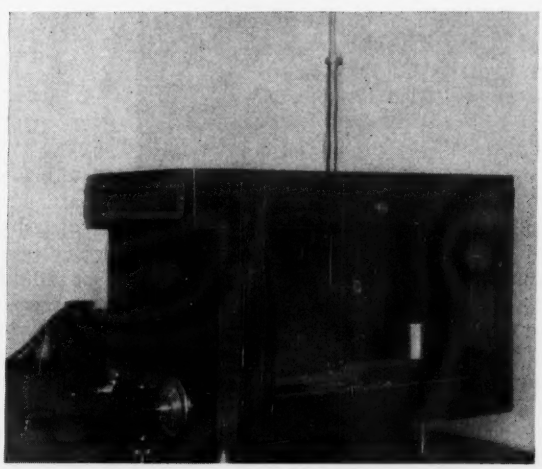


FIGURE 7.—CURIE-CHÉNEVEAU MAGNETIC BALANCE

magnet may be moved forward or backward with respect to the sample, and, because of its magnetic susceptibility the sample is either repelled or attracted depending on whether it is diamagnetic or paramagnetic. The extent of attraction or repulsion is a measure of the magnetic susceptibility. This method is simple and rapid, and the apparatus should not cost much over $200. Relatively small quantities of material are required. On the other hand it is difficult to introduce temperature control, and the sensitivity is not very high. The Curie-Chéneveau balance is of most use in magnetochemical analyses such as are required in rare earth work.

The electron in an atom such as hydrogen is believed to be spinning upon its axis. Because the electron is electrically charged and because it is spinning it protuces a tiny magnetic field as indicated diagrammatically in Figure 8. But when two atoms of hydrogen combine to form the molecule H_2, the two spinning electrons compensate one another so as to produce a valence bond between the two hydrogen atoms and, incidentally, to cancel out the two little magnetic fields. This is indicated in Figure 9. As a consequence of this the molecule of hydrogen is diamagnetic, although atomic hydrogen is paramagnetic. It will be

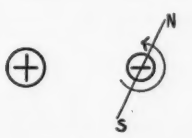


FIGURE 8

Diagrammatic representation of a hydrogen atom, with unpaired electron, and hence paramagnetic.

FIGURE 9

Diagrammatic representation of a hydrogen molecule, with paired electrons, and hence diamagnetic.

noticed that molecular hydrogen must of necessity contain an even number of electrons. This is also true of the vast majority of chemical compounds, which are, as a result, diamagnetic.

Tables of diamagnetic susceptibilities always show a monotonous regularity, seldom exceeding the range -0.2×10^{-6} to -0.8×10^{-6}. Attempts have been made to use the diamagnetism of organic compounds to solve problems of structure and some success in this direction has been achieved by Pascal and by others. But when all is said and done the method has seldom yielded results which cannot better be obtained by other means such as the use of molecular refractivities, based on the refractive index.

Amongst all the chemical compounds known there are scarcely more than a few hundred whose molecules contain an odd rather than an even number of electrons. Yet in the study of these compounds the magnetic method has had great and often brilliant success. Professor G. N. Lewis first predicted that such compounds, often called "odd" molecules, should be paramagnetic. Lewis and Taylor published in 1925 results of experiments showing this prediction to be justified.

When a molecule has an odd number of electrons one of the electrons must of necessity be unpaired. The magnetic field produced by that electron spinning on

its axis must then be uncompensated. Such substances as NO, NO_2, ClO_2, and all organic free radicals such as triphenylmethyl are examples of compounds containing an odd number of molecules. They are all paramagnetic.

The utility of the magnetic method in determining the structure of inorganic molecules will be indicated by two examples. The first is the compound generally known as potassium tetroxide, K_2O_4. If the molecule of this compound is KO_2, then it should contain an odd number of electrons. The number of electrons is obtained by adding up the atomic number of each atom present, in this case $19 + 8 + 8 = 35$, an odd number. Therefore, if the compound is KO_2 it should be paramagnetic. But if, on the other hand, the formula is K_2O_4, then the number of electrons is even, $2 \times 35 = 70$, and the compound should be diamagnetic. Experiment shows it to be paramagnetic and the formula is KO_2, in spite of what most textbooks say to the contrary.

Another example is calomel, and the old question of whether the formula should be written HgCl or Hg_2Cl_2. The first formula would contain 97 electrons, the second 194. Magnetic measurements on the solid and liquid forms of calomel show it to be diamagnetic. The formula, therefore, cannot be HgCl. In the vapor form of calomel the question is more complicated because measurements of vapor density show that it cannot be Hg_2Cl_2 but must be either HgCl or a mixture of free mercury and mercuric chloride, that is $Hg + HgCl_2$. Magnetic measurements have settled this point, too, because even in the vapor form calomel is diamagnetic, proving that the formula HgCl is incorrect in all cases.

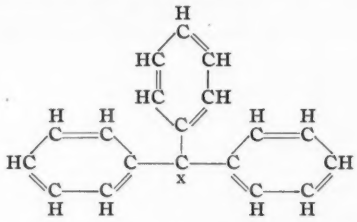
Probably the greatest success of the magnetic method has been achieved in the field of organic free radicals. These compounds were discovered about forty years ago by Professor Moses Gomberg of the University of Michigan. The simplest member of the group is hexaphenylethane which dissociates reversibly into triphenylmethyl, as follows:

hexaphenylethane triphenylmethyl

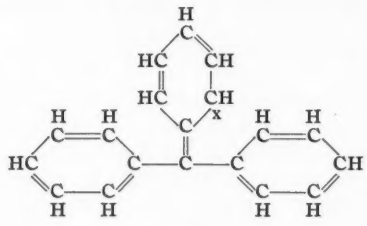
Hexaphenylethane is diamagnetic but the dissociation product, triphenylmethyl, is paramagnetic. Magnetic measurements, therefore, afford a means of determining the degree of dissociation into free radicals at various temperatures and concentrations, in various solvents. The applicability of the magnetic method for this purpose has been amply demonstrated by publications from Professor Eugen Müller in Germany, from Professor Carl S. Marvel at the University of Illinois, and from Dr. L. Michaelis at the Rockefeller Institute for Medical Research.

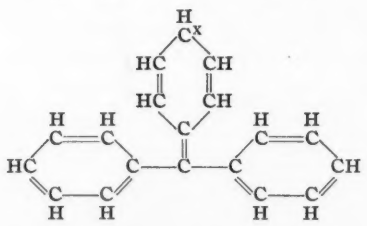
Ever since the discovery of triphenylmethyl scientists have advanced theories to account for the stability of these compounds in which carbon has a valence of three instead of the normal valence of four. One of these theories, the "steric" theory, suggests that the groups attached to the central carbon atom get in the way and so prevent recombination to the corresponding ethane. Others say that the "electronegativity" of the groups determines the degree of dissociation. The theory which has received most attention recently is the "resonance" theory developed principally by Professor Pauling and his associates at the California Institute of Technology.

The following conventional structural formula indicates the free radical triphenylmethyl, an x being used to represent the unpaired electron.



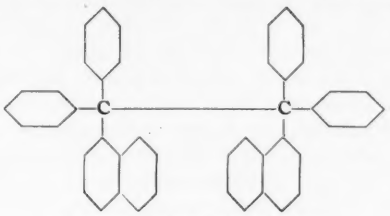
However, the resonance theory implies that the unpaired electron may, with almost equal probability, be found elsewhere in the molecule as indicated below,



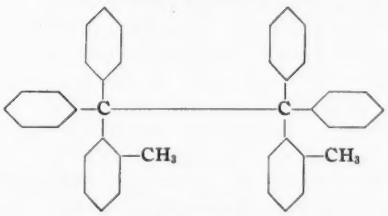


Of course, the electron may also be found on either of the other two phenyl groups. This phenomenon is called "resonance," and if it actually exists as suggested by the theory, it means that additional energy, "resonance energy," is available to stabilize the free radical. The resonance theory has had considerable success in explaining many facts of chemistry. However, recent work by Professor Marvel, and others, tends to throw doubt on the applicability of the resonance theory to explain free radicals. For instance, the resonance theory would predict that the compound di-α-naphthyltetraphenylethane would be considerably more dissociated than di-*o*-tolyltetraphenylethane. This is because of the much greater opportunity for resonance in the first compound. But magnetic susceptibility measurements show that the two compounds are dissociated to about the same degree and require about the same amount of work to dissociate

them, that is, they have about the same heat of dissociation. This and other similar results indicate that



di-α-naphthyltetraphenylethane

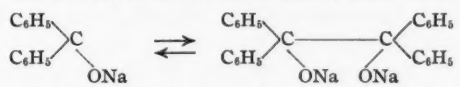


di-o-tolyltetraphenylethane

the resonance theory is inadequate, at least in its present stage of development, to explain all the facts regarding these peculiar compounds.

Another achievement of the magnetic method has to do with the color of the free radicals. Free radical solutions are always colored and it has long been believed that the intensity of the color is a measure of the degree of dissociation. But magnetic measurements have shown that the free radical may be completely destroyed by heating, yet the color of the solution remains exactly the same. Evidently the color of the solution is not only a poor measure of the degree of dissociation, but it may not be related in any way to the presence or absence of free radicals.

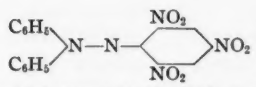
Another type of organic compound, extensively investigated by Müller, is the metal ketyls. If aromatic ketones are treated with metallic sodium in anhydrous ether, they give deeply colored derivatives called ketyls, long suspected of being free radicals in equilibrium with the corresponding sodium benzopinacolate.



a sodium ketyl — sodium benzopinacolate

Müller has shown by magnetic measurements that the majority, if not all, such compounds exist as free radicals, the degree of dissociation running from 3 to 96 per cent.

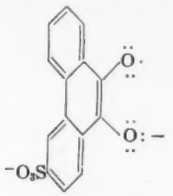
There are some types of free radicals in which the unpaired electron seems to be centered on a nitrogen atom rather than on a carbon atom. The hydrazyls are of this type,



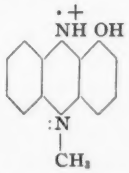
αα′-diphenyl-β-picrylhydrazyl

the particular compound shown being completely in the free radical form even as a solid. Derivatives of nitric oxide such as diphenyl nitric oxide, $(C_6H_5)_2NO$, and similar compounds are also paramagnetic and hence free radicals.

In certain cases the free radical is an ion rather than a neutral molecule. Examples of this are found in the negative semiquinone ion of phenanthraquinone-3-sul-

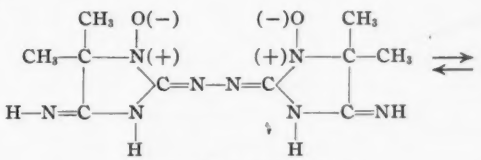


fonate investigated by Michaelis, and the positive semiquinone ion of pyocyanine

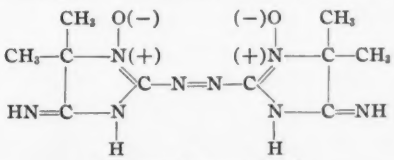


which is derived from the blue pigment of an organism found in purulent wounds.

The existence of molecules containing unpaired electrons raises the question whether or not two such unpaired electrons may not be found in the same molecule. Such "biradicals" have sometimes been postulated to account for reactions in organic chemistry. Proof that such compounds exist has been found by magnetic measurements on several substances, one of which is porphyrindin. This substance exists as a biradical in equilibrium with a diamagnetic form as follows:

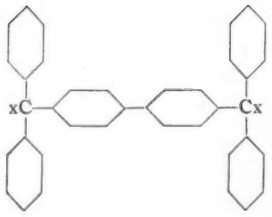


paramagnetic porphyrindin
(Each nitrogen atom marked has only seven electrons.)

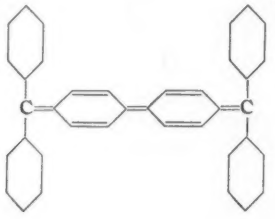


diamagnetic porphyrindin

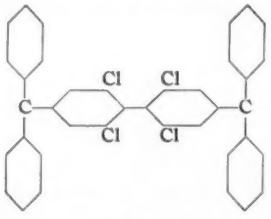
Quite recently Müller has published results of his work on another type of biradical. It would seem that a simple way to make a biradical would be to have two molecules of triphenylmethyl combine at the para position of one of the phenyl groups to form bis(1,4-phenylenediphenylmethyl)



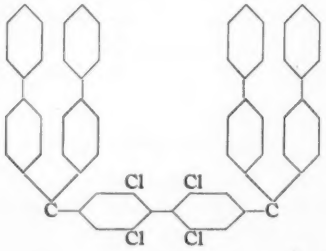
with an unpaired electron at each position indicated. But when this compound is made it is not a free radical because the molecule apparently rearranges to form



in which all electrons are paired. However, this quinoid structure can only be formed if the two central phenyl groups can be brought into the same plane. If, therefore, they can be prevented from lying in the same plane, there is a possibility of obtaining a biradical. Müller has achieved this by putting in groups which prevent free rotation of the two central phenyl groups



as in bis((3,5-dichloro-1,4-phenylene)diphenylmethyl). This compound exists in part as a biradical. While triphenylmethyl is not a particularly stable free radical, trixenylmethyl is much more stable. The final solution to the "biradical" problem came therefore by substituting xenyl groups for four of the phenyl groups in the tetrachloro compound whose formula is given above. This yielded bis((3,5-dichloro-1,4-phenylene) dixenylmethyl)



This compound is at least 80 per cent in the free biradical form at 80°C. in a two per cent benzene solution.

The elements germanium, tin, and lead are in the same group of the Periodic Table as is carbon, and it is not surprising therefore that they should form compounds such as hexaphenyldilead, $(C_6H_5)_3Pb—Pb-(C_6H_5)_3$, analogous to hexaphenylethane. Molecular weight determinations based on boiling point measurements indicate that these compounds are dissociated into free radicals, but magnetic measurements in the author's laboratory show that in no case are any free radicals formed. Measurements were made on the supposed radicals triphenylgermanium, trimethyltin, triphenyllead, and tricyclohexyllead, but in each case the solutions, even at high temperatures, showed no trace of paramagnetism. This work makes it doubtful if any free radical of this type has yet been prepared.

In addition to compounds of the type already discussed it is well known that salts of the transition group elements, especially of the rare earth elements, are often strongly paramagnetic. The ions of transition group elements are generally paramagnetic, not necessarily because they contain an odd number of electrons, but rather because in certain cases the electrons deliberately remain unpaired. Taking the case of iron as an example, the ferric ion has five *3d* electrons. Instead of pairing off to give two pairs and one unpaired electron with a magnetic moment of 1.7 Bohr magnetons, all five electrons remain unpaired so that the ferric ion has a magnetic moment of 5.9 Bohr magnetons. But in the case of the ferrous ion which has six *3d* electrons, two of them pair off, leaving four unpaired with a moment of 5.3 magnetons. In this way the magnetic moments of the ions of the first transition group rise from zero with the Ti^{++++} ion to a maximum of 5.9 with Fe^{+++}, and then fall to zero again with the Cu^{+} ion.

Salts of ferric iron in general have a magnetic moment of about 5.9, but in iron coördination complexes the situation may be somewhat different. In a covalent octahedral complex two of the five *3d* orbitals are required to complete the valence bonds of the iron with the coördinating groups. Consequently only two *3d* orbitals are available for the five *3d* electrons which must therefore form two pairs and one unpaired electron. The magnetic moment of such a complex should therefore be about 1.7 magnetons. If, however, the bonds of the complex are ionic in character, then the magnetic moment will remain at 5.9. The moment of $K_3Fe(CN)_6$ is 2.33, indicating that the bonds are largely covalent. But the moment of $(NH_4)_3FeF_6$ is 5.9, indicating that the bonds are essentially ionic. In this way magnetic measurements may often be used to determine the kind of valence bond in a complex molecule. Thus in prussian blue some of the iron atoms are shown to have ionic bonds while others are essentially covalent.

In some cases it is possible to decide between spatial configurations of coördination compounds by means of magnetic measurements. Much progress in this direction has been made by Professor Pauling and his associates. An excellent summary is given in his book

"The Nature of the Chemical Bond." Of particular interest is the structure of hemoglobin and its derivatives as worked out by Pauling and Coryell.

Another quite different application of magnetic methods is in the structural study of such compounds as nickel sulfide or nickel oxide. It has long been assumed that the formulas of these compounds are properly written as NiS and NiO, respectively. But measurements by Klemm and others in Germany show that a substance analyzing exactly for the formula NiO has a magnetic susceptibility near that of metallic nickel; in other words it contains metallic nickel. But if the substance is prepared with a very slight excess of oxygen then the susceptibility immediately falls to a normal value for the compound. It appears that the compound NiO has no existence unless about 0.5 per cent excess oxygen is present. Similar results have been found with other compounds.

Within the last few years there has appeared a number of papers dealing with the structure of catalytically active surfaces as determined by magnetic measurements. Hüttig and his associates in Germany have published over one hundred papers bearing on this topic. The kind of information obtainable will, however, be illustrated by a single example of work carried out in the author's laboratory.

Pure copper is a very poor catalyst for the hydrogenation of benzene, but copper on which is dispersed about one per cent of nickel becomes a very good catalyst. If this mixture is heated to about 400°C. for several hours it loses its catalytic activity. The questions then arise: in what state is the nickel when it is active, and what happens to it when its activity is destroyed?

Pure copper is slightly diamagnetic and its magnetic susceptibility is independent of field strength. Nickel is strongly ferromagnetic when it exists as metallic nickel, but dilute solid solutions of nickel dissolved in copper are only paramagnetic, that is, the susceptibility is no longer dependent on the field strength.

An active catalyst was prepared and it proved to be strongly ferromagnetic. This proves that the nickel is not combined with or dissolved in the copper, and it is not in an atomic state of subdivision because individual atoms of nickel are not ferromagnetic. In other words, the nickel is present as micro-crystals of metallic nickel on the surface of the copper. Now, as shown in Figure 10, if the catalyst is heated until it loses its catalytic activity, it also loses most of its ferromagnetism. This proves that the heating process promotes diffusion of the nickel into the copper and that a catalytically inactive solid solution has been formed. The reason that heat inactivates the catalyst is because the nickel dissolves in the copper.

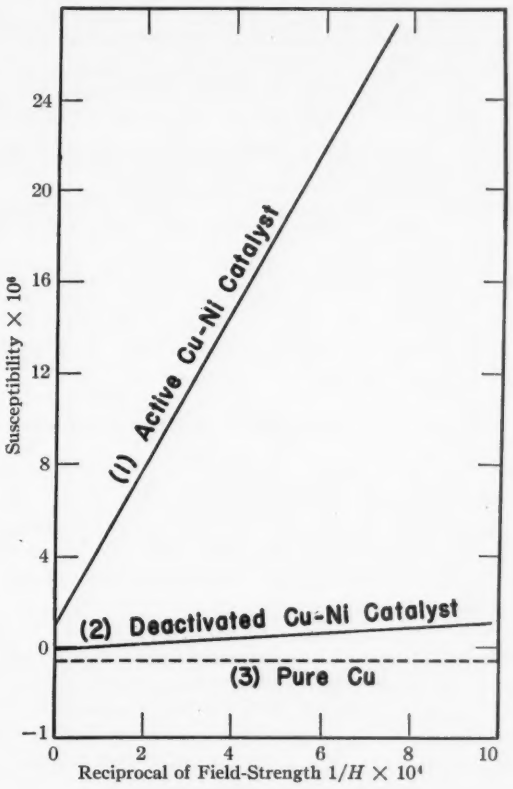


FIGURE 10

Showing ffeld-strength dependence of magnetic susceptibility for (1) an active catalyst consisting of 1% nickel on copper, (2) the same mixture after thermal inactivation, and (3) pure copper.

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Ammonia

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HISTORICAL BACKGROUND

AMMONIA is one of the by-products obtained when coal is carbonized in a gas retort or a coke oven. Coals such as ordinarily used in gas or coke plants contain about 1.4 per cent of nitrogen. If all this nitrogen were recovered as ammonia in the carbonization of coal, the average yield would be about 34 pounds of ammonia per ton of coal processed. Some of the nitrogen is not driven out of the coke, however, and not all that is volatilized is recovered in the by-product plant. The actual yield is only about 5 pounds of ammonia per ton of coal coked.

When the manufacture of coal gas and coke was first undertaken on a commercial scale, in the early decades of the nineteenth century, the disposal of the tar, ammonia, and volatiles other than the gas presented a difficult problem. As time passed, uses were found for these once troublesome by-products. So far as the ammonia was concerned, it became one of the chief sources of nitrogen for agricultural fertilizers, rivaling in importance the Chilean nitrate which also came into use in agriculture early in the last century.

The quantity of by-product ammonia available was, of course, limited by the fact that it was produced only to the extent that coal gas and coke were needed. The coal carbonizing industry grew rapidly during the nineteenth century, but so did the agricultural and the industrial demands for ammonia, so that a market was never lacking.

Aside from its use in manufacturing fertilizer, ammonia found increasing uses in industry during the nineteenth century. In particular, the development of ammonia-filled refrigeration systems gave by-product ammonia a new outlet. But most of the by-product ammonia has always been used in agriculture. The method of recovery used at coal gas and coke plants is to absorb the ammonia gas either in water to form aqua ammonia, or in sulfuric acid to form ammonium sulfate which is then sent to fertilizer manufacturing plants.

After the establishment of cyanamide plants such as previously described elsewhere,[1] a small part of the total cyanamide produced was converted to ammonia, but the production of ammonia by this method was too small to change the general situation. With the development of the direct synthetic ammonia process early in the twentieth century, the situation changed. During World War I, Germany built large plants for the production of synthetic ammonia, and immediately after the war other nations did likewise. By 1926 the monopoly control of the prices of fixed nitrogen by the Chilean nitrate industry was broken, and since that time world market prices for fixed nitrogen have been set by the price of ammonia. Ammonia has become a commodity of world trade. Fixed nitrogen in the form of ammonia has become the cheapest fixed nitrogen available. Ammonia is therefore the raw material from which many other nitrogen compounds are manufactured, and ammonia has become one of the basic chemicals of chemical industry. A few of the many ways in which it is used will now be discussed.

USES OF AMMONIA

Ammonia as such is still the material most widely used in refrigeration systems. Ammonia is also used directly for the "ammoniation" of superphosphate for agricultural application. Ammonia in water solution is used as an alkaline medium in many processes where the hydroxides or carbonates of the alkali metals were formerly used. And where relatively small volumes of hydrogen are desired, it is often economical to obtain the hydrogen by the "cracking," *i. e.*, thermal decomposition, of ammonia to form a mixture of three volumes of hydrogen to one of nitrogen. For most purposes the presence of the inert nitrogen is not objectionable.

Considerable quantities of ammonia are used to produce the various ammonium salts, such as the ammonium chloride used in electric dry cells, the ammonium sulfate and ammonium phosphate used as a fertilizer, the ammonium nitrate used in explosives, etc.

CONVERSION OF AMMONIA TO NITRIC ACID

Nearly all the nitric acid used in industry is now made by the oxidation of ammonia to nitric oxide by means of air, and the subsequent conversion of the nitric oxide to nitric acid by the same process as was discussed previously.[1] The oxidation of ammonia may be represented thus:

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

This reaction is accomplished by passing a mixture of ammonia and air through a fine-mesh platinum gauze maintained at a temperature of about 900°C. The platinum acts as a catalyst. The heat liberated by the reaction is almost enough to keep the gauze at the desired operating temperature. The additional heat is supplied by warming the air before mixing it with the ammonia.

Nitric acid is an important compound in chemical industry. Concentrated nitric acid, mixed with concentrated sulfuric acid, is used in nitrating certain organic compounds which are then used in manufacturing dyes. Likewise, glycerin may be nitrated to form the explosive nitroglycerin. Nitroglycerin, usually mixed with ammonium nitrate, is used in manufacturing dynamite. Cotton linters may be nitrated and the product made into cellulose plastics, synthetic fibers such as rayon, or into smokeless powder which has now replaced ordinary gunpowder. By nitrating toluene, the explosive TNT (trinitrotoluene) is manufactured. A mixture of TNT and ammonium nitrate is used for certain types of military explosives. Ammonium nitrate is manufactured from ammonia and nitric acid, the latter being produced from ammonia as indicated above.

Aside from its use in the production of dyes and synthetic fibers and explosives, nitric acid derived from ammonia is used in the manufacture of all the nitrates used in industry, such as potassium nitrate, silver nitrate, nickel nitrate, ferric nitrate, copper nitrate, etc. Even sodium nitrate for agricultural use is produced from synthetic nitric acid and sold in competition with the natural sodium nitrate from Chile.

Before the advent of cheap ammonia, the nitric acid used in industry in all the ways indicated above was produced by treating Chilean nitrate with sulfuric acid. This process has the advantage that it yields concentrated nitric acid directly whereas the ammonia process of manufacturing nitric acid yields an acid of not more than 60 per cent strength. This dilute acid must be concentrated if "nitrating acid" is to be made, but since ammonia can now be produced so cheaply it is more economical to use ammonia for the production of relatively dilute nitric acid and then to concentrate the acid, than it is to produce strong nitric acid directly from Chilean nitrate.

CONVERSION OF AMMONIA TO UREA

By treating carbon dioxide with ammonia under suitable conditions urea may be produced thus:

$$CO_2 + 2NH_3 \longrightarrow CO(NH_2)_2 + H_2O$$

Urea is used industrially for the production of some of the synthetic plastics which are now widely used. Urea is also used in the production of nitrogenous fertilizer mixtures.

AMMONIA IN THE NATIONAL WAR PROGRAM

As indicated before,[1] the discovery and use of gunpowder created an ever-growing demand for potassium nitrate. At first this potassium nitrate was laboriously collected from small deposits over the world. After the discovery of the Chilean deposits of sodium nitrate and the Stassfurt deposits of potassium chloride and potassium sulfate, the much desired potassium nitrate could be produced by simple chemical processes using these raw materials.

Gunpowder, or "black powder," is an intimate mixture of sulfur, charcoal, and potassium nitrate. When ignited it burns very rapidly, yielding, among other things, large volumes of gases which are heated to high temperatures by the heat liberated in the burning. The pressure rapidly developed by the gases, if they are confined, gives black powder its value as a blasting material and as a propellant in gun barrels.

The newer types of explosives which came into use during the closing decades of the nineteenth century differ from black powder in many ways. They are not mixtures of combustible materials, such as charcoal and sulfur, with oxidizing agents, such as potassium nitrate. For the most part they are nitrated organic compounds and are of two classes. The propellants, such as smokeless powder, burn rapidly, giving only gaseous products. Their action is therefore similar to that of black powder. The other class, the so-called high explosives, may be "detonated," *i. e.*, they may be induced to decompose with enormous rapidity, yielding gaseous products so suddenly that a very sharp and very powerful compression wave is set up. Damage caused by high explosives is not done primarily by the pressure of the expanding gases produced, but by the impact of the detonation wave.

Inasmuch as large quantities of both propellants and high explosives are used in modern warfare, a national war program, such as the one in which the United States is now engaged, makes it necessary to build several new ammonia plants, along with plants for manufacture of smokeless powder, TNT, and other military explosives. All the new ammonia plants will use one of the direct synthetic processes described previously.[1]

Some of the ammonia will be used as such in the manufacture of the explosives ammonium nitrate and ammonium picrate, but most of it will be converted to nitric acid for the nitration of such organic compounds as cotton, toluene, aniline, etc., in making the corresponding military explosives.

[1] CURTIS, "Nitrogen fixation," J. CHEM. EDUC., **19**, 161 (1942).

Electrical Properties of Solids[1]

Part I

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FROM the point of view of classical electrostatics, solids may be divided into two general classes, conductors and insulators. The ideal conductor can by definition support no difference in potential; that is, if one point of a conductor is brought to a given potential, the entire conductor assumes that potential. The classical dielectric, on the other hand, is a medium in which a potential difference can permanently store a charge proportional to itself. In practice, of course, we never find these ideal limiting cases. Solids, as we know them, are divided into conductors, semiconductors, and insulators according to the magnitude of their D.C. conductivities.

Roughly speaking, conductors are those solids for which the conductance is 10^3 reciprocal ohms per centimeter or higher, and includes the metals and most of their compounds and alloys. The mechanism of conductance is transfer of electrons. Silver, for example, has a conductance of 6.7×10^5 at 0°; that is, it would take nearly four miles of silver one centimeter square to give a resistance of only one ohm. It thus approaches the ideal conductor very closely; however, in the form of thin films or fine wires, fairly high resistances can be made of silver.

Insulators are those solids for which the conductance is of the order of 10^{-10} reciprocal ohms per centimeter or less. Diamond, fused quartz, and sulfur with conductances of the order of 10^{-18} or less are the "best" insulators, in the sense that a condenser, in which one of them was the dielectric, would retain its charge the longest and on continuous use on A.C. would develop the least heat. Other familiar insulators are the hydrocarbons, such as paraffin, rubber, and polystyrene. For treatment in later discussion, it is convenient to divide insulators into ionic, polar, and non-polar. The ionic insulators, such as rock salt, are insulators at low temperatures and conductors at high. Both polar and non-polar insulators, if free from electrolytic impurities, are insulators from the D.C. point of view, but polar dielectrics can, under certain conditions to be discussed later, become poor dielectrics from the A.C. point of view in that they develop heat on continuous use on A.C. The difference between insulators for A.C. and D.C. use lies essentially in the difference between the two kinds of current. For a D.C. current to flow, it is *necessary* that there be a unidirectional *transport* of charge either as ions or electrons. But a *periodic displacement* of charges about equilibrium positions is *sufficient* for the existence of an alternating "current." Consequently mere electrical asymmetry, induced by the field, or permanently resident in the molecule, will permit the production of an alternating current under the influence of an alternating E.M.F. If the periodic displacement is out of phase with the applied E.M.F., the absorption current will cause heat losses in the dielectric. Many of the polymeric insulators, such as phenol-formaldehyde resins, polyacrylates and other polyesters, cellulose and its derivatives, and so on all exhibit this form of power absorption under suitable conditions of temperature and frequency, even though their D.C. resistance may be very high.

Between the metals and the practical insulators, that is, between conductances of about 10^3 and 10^{-10}, are included a large number of solids called semiconductors. The conductance in some cases (for example, silver halides and other salts) is ionic, and in others electronic (for example, many oxides).

To summarize our classification of solids, we have then metallic conductors with low D.C. resistances, insulators with high D.C. resistances and the possibility of high or low A.C. absorption according to whether they are polar or non-polar, and semiconductors, both ionic and electronic, with intermediate D.C. resistances. Most of the first session will be devoted to a necessarily condensed account of some of the properties of metals and semiconductors. Then after a review of the Debye theory of dispersion and absorption in polar systems, we shall turn to a consideration of insulators, paying especial attention to polymeric systems.

Both metals and electronic semiconductors can be treated from the point of view of the quantum theory; in fact, as we shall see shortly, the density of population of electron energy levels and their relative spacing permits an exact definition of conductor, semiconductor, and insulator, as far as electronic processes are concerned. We must not think that some substances are insulators, merely because their electrons are firmly bound to nuclei, because electrons can tunnel through appreciable potential barriers at atomic distances, and electronic conduction would be possible in general, with only a range of several decades between high and low limits, instead of some tens of decades as is actually the case. The availability of mobile electrons is necessary to electronic conductance, but not sufficient; they must also have a permitted place to move to. Several examples will make this point clearer.

The possible states of an electron in a lattice are divided into zones, in which the energy levels form continuous bands. These zones are in general separated by intervals of forbidden energy ranges of various widths in different crystals, although in some cases they may overlap. If the zone of lowest energy is completely occupied by electrons, and the zone of next highest energy permitted does not overlap this zone,

[1] Lecture given at Brooklyn Polytechnic Institute, Brooklyn, New York, January 31, 1942.

then the crystal will be an insulator at absolute zero, because the only possible electron motion is interchange and this cannot give rise to a current. As the temperature increases a few electron transitions to higher levels may become possible, and then we have a semiconductor, in which the conductance increases with increasing temperature. If the energy gap separating the filled zone from the nearest empty zone is large, then thermal energy in the usual range of kT values will not suffice to raise electrons to higher zones, and the substance will be an insulator over a wide range of temperature. If, on the other hand, the lowest zone is not completely filled, then there are more permitted states than there are electrons, and we have metallic conduction. So, for example, with the monovalent metals which crystallize in the cubic system—the alkalies, copper, silver, and gold. Here there are 2 N possible states and N electrons per gram atom, the 2 being due to the two possible spin directions of the electron. Then the small additional potential energy imparted to an electron by an external field is sufficient to cause an electron current to flow and normal metallic conduction appears. In the case of the metals immediately following the monovalent metals in the periodic series, we have 2 N electrons and 2 N states in the lowest energy level. Their conductance is lower than that of the monovalent metals; that they conduct at all is evidence that the next highest zone overlaps the first, so that electrons can move in the crystal under the influence of an external field. The mere fact that a system contains only metallic atoms is not sufficient for metallic conductance; for example, alloys like Mg_2Sn, Mg_2Pb, and others which crystallize with the fluorspar structure have very high resistances. Here we have 12 atoms per unit cell, with 32 valence electrons, and calculation shows that the Brioullin zone has only 32 states, in agreement with the low observed conductivity. That this situation is actually due to conditions imposed by structure is shown by the fact that on melting (which destroys the fluorite structure), the resistance of these metallic compounds drops abruptly to about that of molten tin.

It was recognized very shortly after the discovery of the electron that metallic conduction was due to the presence of free electrons in metals. Classical theory was able to account for some of the properties of metals immediately, but it also encountered difficulty, especially in the temperature coefficient of metallic conductance and in the specific heats. If we assume that the conductance of a monovalent metal is due to free electrons, then, on the basis of the classical theory, we should also have to assume that each electron had a mean kinetic energy of $^3/_2kT$, which would lead to a specific heat for the metal of twice the classical Dulong and Petit value. Consequently, classical physicists found themselves in a dilemma; they wanted free electrons in metals to account for the electrical conductance, but could not give them any kinetic energy on account of the specific heat.

The classical picture of the mechanism of metallic conductance was an electron accelerated by an external field ($m\ddot{x} = Ee$) for an average time 2τ, after which it would collide, be stopped, and start over again. The average velocity would then be

$$Ee\tau/m = u$$

giving

$$j = Neu = ENe^2\tau/m$$

for the current and

$$\kappa = Ne^2\tau/m$$

for the conductance. A mean free path l between collisions was set equal to $2\tau u$, and assuming that the electrons in a metal behaved like molecules of a perfect gas, Boltzmann statistics gave

$$^1/_2mu^2 = (^3/_2)kT$$

whence

$$\kappa = Ne^2l/2mu = Ne^2l/\sqrt{3mkT}$$

This formula gave the right order of magnitude of conductance for, say, silver at room temperatures, if l was taken of the order of atomic distances. But the formula calls for a decrease of conductance with increasing temperature as $T^{-1/2}$ and actually it decreased as $1/T$ in the ordinary range of temperatures. To save the situation, Lorentz and Drude were forced to assume that the mean free path increased as T decreased, which did not seem reasonable on the basis of classical statistics. Furthermore, the conductance of metals increases with increasing pressure at fixed temperature, and one would intuitively expect the mean free path to decrease on compression.

The one outstanding success of the classical theory was the derivation of the Wiedemann-Franz law, which states that the ratio of thermal to electrical conductance is proportional to T, with the same constant of proportionality for all metals. Since both processes are transport problems, we realize now that the correct answer came out by a compensation of errors: the mean free path difficulty divided out of both sides of the equation. Another difficulty on the basis of the classical theory was an explanation of the large increase in resistance caused by relatively small amounts of impurities in metals.

Time, of course, does not permit a detailed exposition of the quantum theory of metallic conductance, but we can at least review the important points. The first advance was made by Wien, who proposed that the mean free path was inversely proportional to the mean square amplitude of the atomic vibrations. Sommerfeld was the first to apply Fermi-Dirac statistics to the electrons in a metal. On the basis of these statistics, all energy levels for electrons up to the maximum energy are occupied at absolute zero, and all states above this are empty. Sommerfeld assumed that the potential in a metal was uniform, which is equivalent to saying that a given electron is acted on by the time *average* field of the nuclei and of all the other electrons; this averaging is permitted on the basis of wave me-

chanics. Of course, there is a singularity in potential at each nucleus, but roughly speaking, the electron does not stay there very long. The use of Fermi-Dirac statistics eliminated the specific heat paradox, and justified the idea of a mean free path for electrons which was not related to their mean kinetic energy. Bloch improved Sommerfeld's calculation by allowing for the periodicity of the field in the lattice. The important result of the calculations is that, in a uniform or a periodic field, a beam of electrons once set in motion will continue to move indefinitely: in other words, all metals would be supraconductors if the lattices were perfect and the periodicity undisturbed.

In a real crystal, however, thermal motion disturbs the perfect periodicity of the lattice and the moving beam of electrons is scattered. This is the fundamental reason for the finite resistance of metals on the basis of the quantum theory. If we take an Einstein model of the crystal for simplicity, where each atom vibrates about its mean position with a characteristic frequency ν, and the restoring force is b, we have for the equation of motion of an atom

$$M\ddot{X} = -bX, \text{ or } b/M = 4\pi^2\nu^2$$

and since

$$\nu = k\theta/h$$

where θ is the Einstein characteristic temperature,

$$b = 4\pi^2Mk^2\theta^2/h^2$$

If X^2 is the mean square displacement of an atom, it measures its effective scattering power for electrons in that it is a measure of its target area. For $T > \theta$,

$$^1/_2bX^2 = {}^1/_2kT$$

and since the resistance is proportional to the scattering probability, which is in turn proportional to X^2, we have

$$R \sim X^2 = \frac{kT}{b} = h^2T/4\pi^2Mk\theta^2$$

$$R \sim T/M\theta^2$$

Thus we have the correct high temperature relationship between resistance and absolute temperature, and furthermore a correlation between electrical, thermodynamic, and elastic properties through the appearance of θ in the above equation.

A more careful calculation, using the Debye distribution, does in fact give good agreement—for example, θ for lead is 88° from specific heat data and 92° from conductance; 215° for silver from specific heat and 230° from conductance, etc. The calculation sketched above holds, of course, only for the high temperature range, where

$$^1/_2bX^2 = {}^1/_2kT$$

For lower temperatures, the more exact

$$(^1/_2)bX^2 = \frac{^1/_2h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

must be used. Proper application of this partition function leads to an explanation of the very rapid decrease of resistance at very low temperatures, much in analogy to the way the specific heat of crystals drops as the temperature becomes low.

The increases in resistance due to small amounts of impurities and on melting are also, qualitatively at least, seen to be caused by disturbances in the periodicity of the lattice. In the former case, a foreign atom in the lattice disturbs the field distribution and in the latter, the regular lattice is destroyed.

We next turn to the semiconductors. Here two cases must be clearly distinguished: the electronic and the ionic. Mixed types also occur, of course. We shall first consider the electronic semiconductors, because they are treated from the same point of view as the metals: a drift of electrons in the potential field of a lattice under the influence of an external field. As we have already shown, the fundamental difference between a conductor and a semiconductor is the availability of energy states in a given Brioullin zone. In the metal, energy states are available in the zone of lowest energies, while in semiconductors, the number of states equals the number of electrons; and in order to be free for electrical conductance, an electron must be raised to a higher energy state by thermal excitation. It is also possible to raise an electron to a higher energy state by photo excitation or to give it the necessary energy by means of a very high intensity field.

From this point of view, of course, the difference between insulators and semiconductors is merely one of degree—in an insulator, the gap of forbidden energies between the lowest filled zone and the next highest zone is very large on an energy scale measured by kT; while for semiconductors, the difference corresponds to kT's with T of the order of hundreds or, at most, a few thousand degrees. This requirement of thermal activation is one of the characterizing differences between metallic conduction and semiconduction, because it leads to a decrease of resistance with increasing temperature for semiconductors. Ionic conductance also increases with increasing temperature, usually exponentially. Only for metals does the conductance increase with decreasing temperature. The outstanding difference between metals and other substances is naturally the magnitude of the conductance, which is, with only a few exceptions, many million times larger than that of other materials.

There are three general types of electronic semiconductors: defect or oxidation semiconductors, excess or reduction semiconductors, and intrinsic semiconductors. In order to simplify the exposition, a typical member of each group will be discussed.

An intrinsic semiconductor is one which satisfies the simplest condition outlined above for the existence of semiconductance—a completely filled lowest energy band, and an empty band nearby, into which thermal excitation can drive electrons. Copper oxide, CuO, is an example of this group. According to Fermi statistics, the number of electrons in the upper band is given by

$$N \exp(-E/2kT)$$

and here E is of the order of a few tenths of an electron volt, so that sufficient electrons are present in the conducting band to carry a small current. Iron oxide, Fe_2O_3, is similar, $\kappa \approx 10^{-8}$. Magnetic oxide, $Fe_3O_4 = FeO \cdot Fe_2O_3$, is also an intrinsic semiconductor with a rather high conductance ($\kappa \approx 10^2$); it owes its high conductivity to a special mechanism. Ferrous and ferric ions are statistically distributed over equivalent lattice points, and the conductance is due to electrons migrating from ferrous to ferric ions.

The excess and defect semiconductors are also called extrinsic semiconductors, because they owe their existence to impurities (either ions or holes, or interstitial ions) in the lattice. Incidentally, we see here another fundamental difference between metals and electronic semiconductors—impurities decrease the conductance of metals and raise the conductance of electronic semiconductors. The reason is fairly easy to understand: the energy levels in a foreign atom are in general different from those in the lattice atoms. Hence the foreign atom may furnish electrons to the conduction band of the lattice, or it may accept electrons from the normal lattice ions leaving empty electronic states for other lattice electrons and thus permit conductance. We must always keep the fundamental principles of electronic behavior in mind: electrons in a completely filled band cannot conduct, but only electrons in a partly filled band. In metals this band is present *a priori;* in semiconductors it is reached by excitation or provided in some way by lattice defects.

In the case of oxidation and reduction semiconductors, the defects are not foreign atoms in the lattice. Cuprous oxide is a typical oxidation or defect conductor—its conductance increases with the partial pressure of oxygen. Cuprous ions on the surface are oxidized to cupric, when an oxygen atom reacts to form an oxygen ion. The oxygen ion is too large to fit between lattice points, and it cannot substitute for a copper ion—hence each oxygen ion formed creates two cupric ions and two vacant spots in the cation lattice. The defect of electrons in the cupric ions gives energy levels into which electrons from cuprous ions can enter, and thus permits conductance. The normal diffusion in the crystal distributes the holes and the extra oxygen atoms.

Zinc oxide is a typical excess or reduction semiconductor—its conductance decreases with increased oxygen pressure. At 600° or higher, ZnO is partially dissociated, and some oxygen escapes, leaving an excess of metal behind. Since the zinc atoms are small compared to oxygen ions, they probably take up interstitial positions, rather than creating holes in the anion lattice. The excess electrons in the zinc atoms are now in the conductance band, and again we get electronic conductance.

Copper halides are defect conductors—their conductance rises with increased partial pressure of halogen. With cuprous iodide, for example, iodine atoms enter the lattice, form iodide and cupric atoms, and produce holes in the cation lattice. As in the case of CuO, the cupric ions have vacant energy levels which permit electron migration.

The case of ionic semiconductors can be treated entirely from the classical point of view. Here we simply have an ionic lattice, such as Ag^+ and I^- ions in silver iodide, or Pb^{++} and I^- ions in lead iodide. Diffusion in solids is, of course, much slower than in liquids, but it does occur at a measurable rate. This can be demonstrated in a very pretty way experimentally, using radioactive isotopes. Formerly, the experiment could only be performed with lead, which has Thorium B as an active isotope, but now, thanks to the cyclotron, we have available radioactive isotopes of many elements. In order to study the self-diffusion of lead, for example, lead containing radioactive lead was placed in close contact with ordinary lead, and after some time, the ordinary lead was found to contain active lead. By studying the intensity of the radioactivity as a function of depth, the rate of diffusion could be determined. Then the mobility u, which is the coefficient of proportionality between migration velocity and field strength, is given by the Einstein relationship: $D = kT/u$, where D is the diffusion constant.

The electrolytic conductance of ionic crystals is due to a component of velocity in the field direction which is superimposed on the random self-diffusion of the ions in a lattice. If the mobilities of the two ions are equal, both ions contribute equally to the current, as in PbI_2; if one has a much higher mobility, it will carry most of the current. In other words, the Faraday equivalence law and the laws of transference numbers, which hold for solutions of electrolytes and for fused salts, are also applicable to solid crystals.

A typical experiment in ionic semiconduction is made as follows. A platinum cathode and a silver anode are pressed tightly against three buttons of silver iodide, and the cell is put in series with a silver coulometer and a voltage source. After running the current for some time, the cell is disassembled and the parts weighed. In this case, the anode lost a weight of silver equal to that deposited in the coulometer and an equal amount was deposited on the platinum cathode. The weights of the three silver iodide blocks were unchanged. Here we have a clear case of ionic conductance, where the silver ion has transference number unity and the iodide ion practically zero. (If the iodide ion carried an appreciable amount of current, the AgI button adjacent to the cathode would have lost weight and the anode AgI button would have gained the same amount.) And if any electronic conductance had been present, the reaction products at the electrodes would have been less than the electrochemically equivalent amount of silver appearing in the coulometer. Experimentally, this is the method of distinguishing between ionic and electronic conductance—if the electrochemical reaction at the electrodes is given by Faraday's law, the conductance is entirely ionic; if less, it is partly electronic; and if there is no electrode reaction, the conductance is entirely electronic.

(To be continued.)

High-School Chemistry

Activated Carbon

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WHEN charcoal, or other carbonizable substances, are prepared (activated) under the proper conditions of heat or chemical treatment, they acquire an unusual property which can be demonstrated in the following simple experiment:

In a glass of water, dissolve two or three pieces of striped peppermint candy. Filter the solution through filter paper in an ordinary glass funnel. Observe that such filtration does not remove either the color or peppermint flavor. Now add to the filtered solution about a half teaspoonful of activated carbon, and stir this actively for five minutes. Filter out the carbon, and note that both the color and flavor have been removed, although the sweet taste of sugar is still present.

This little experiment involves, on a small scale, a process which is used industrially on a very large scale.

The white sugar we use daily is obtained from either sugar cane or sugar beets, where it occurs dissolved in the juices of the cane stalk or beet root. These juices also contain many other substances which must be removed before the final step of crystallizing out the pure sugar. The process of refining sugar is concerned mainly with the removal of these impurities.

A considerable portion of the impurities can be removed by ordinary filtration, and by other means which need not concern us here in detail. However, there will remain in solution with the sugar certain colored impurities, and also a class of complex non-colored substances known to the chemist as colloids, which can be removed only by means of activated carbon.

Courtesy of the Atlas Powder Company

AT MEAL TIME, ACTIVATED CARBON IS OUR UNSEEN SERVANT. IT IS USED IN THE REFINING OF SUGAR.

Replace the drinking glass of our experiment with a tank of several thousand gallons capacity, install in the tank a motor-driven paddle on a shaft for mixing, and provide a filter press, pipe lines, and pump to substitute for our glass funnel and filter paper, and we are ready to repeat our experiment on an industrial scale. After the tank has been filled with sugar solution coming from a previous processing step, powdered activated carbon is added, stirred with the solution for a sufficient time, and then removed by pumping the solution through the filter press.

The filtered solution will have little or no color or colloidal impurity remaining in it, and can now go through the vacuum evaporating process whereby the sugar is crystallized out in clean, well-formed grains.

In an older process which is still extensively used, the sugar solution is percolated through beds of granular carbon in large towers. The carbon used in such towers is made by carbonizing animal bones coming from the meat packing industry and is known as bone char or bone charcoal.

There are many other industries which use activated carbon in preparing pure finished products from materials of plant, animal, or synthetic origin. Quinine from cinchona bark and caffeine from coffee or tea are examples of medicinal products; pectin, gelatin, vinegar, wine, cottonseed oil, and numerous other oils and fats are among the other food products besides sugar. Citric, tartaric, lactic, gallic, and oxalic acids are so purified; likewise, uncountable chemical products which are employed in the manufacture of dyes, plastics, nylon, cellophane, tooth paste, shaving cream, cosmetics, photographic developers, and other indispensables of our complex modern civilization. In practically all of these the powdered form of activated carbon is used.

Another very large field of application is in the treatment of water supplies. Water in streams, lakes, and reservoirs may acquire disagreeable tastes and odors arising from decayed vegetation, microscopic organisms known as algae, or from the discharge of industrial waste effluents. Such odors and tastes can in practically all cases be removed by the addition of surprisingly small amounts of powdered carbon (ordinarily twenty to thirty pounds per million gallons is enough). The treatment is conducted at the "water refinery," *i. e.*, the municipal filtration plant, which also removes suspended matter from the water, makes it bacteriologically safe for human consumption, corrects any tend-

ency of the water to corrode pipe lines, and when necessary may soften it to make it more suitable for domestic and industrial use.

Activated carbon is frequently useful also in maintaining the purity of liquids that become contaminated with continued use, as is the case with liquids used in the "dry" cleaning of clothes. The petroleum distillates or chlorinated hydrocarbon solvents used for this purpose acquire color and odor from the clothes cleaned in them, and must be purified continuously to maintain their usefulness. Similarly, the solutions used in industrial electroplating become contaminated with impurities that interfere with the deposition of a bright, smooth, adherent metal plate. Activated carbon treatment removes many such impurities.

Different activating processes are used in making carbons that are suitable for various classes of use. All the uses described heretofore deal with carbons suitable for the purification of liquids, and within this general field considerable variation in activation processing is necessary.

A somewhat different activating process produces the so-called "gas adsorbent" carbons. These were prominent before the public attention during the last World War, when they were urgently needed for use in gas masks. Such carbons find extensive industrial use, when it is necessary to remove an undesirable impurity from a gas, as in the manufacture of "dry ice," or more frequently, when a valuable material in vaporized form is to be recovered from air or from other gas mixtures. For example, in the lacquer spraying of automobile bodies considerable valuable solvent can be lost into the air in vaporized form. The spraying is done in ventilated booths, however, where the air and solvent vapor are drawn off by means of a fan and passed through beds of activated carbon which "select" the solvent while allowing the air to pass on. When the carbon bed has taken up as much solvent vapor as it can hold, it is steamed out and the solvent is recovered as a liquid by condensation from the steam. Very dilute air-solvent vapor mixtures can be so treated with substantially complete recovery of solvent.

In the manufacture of activated carbon, the most commonly used raw materials are lignite, wood or wood charcoal, and lignin-bearing waste residues of the paper industry. Any carbonizable material can be used subject to such economic considerations as price, availability, purity, obtainable yield of carbon, and transportation cost.

The primary object of activation is to produce a carbon of optimum porosity. By means of heat or chemical treatment, or both, a carbonizable material is so handled that it emerges with myriads of sub-microscopic pores leading into a complex internal network of similarly tiny passages. A solid so prepared is substantially all surface, within a proportionately small rigid volume. It is this enormous surface, properly conditioned, which gives activated carbon its peculiar "adsorptive" properties.

After activation, which is usually conducted on coarse particles, the carbon is crushed and screened to secure an optimum distribution of particle shapes and sizes. This is necessary so that, in powdered form, the carbon may be adequately dispersed in the liquid to be treated, and yet readily filtered out after treatment has been completed. Gas-adsorbent carbon, mostly employed in granular form, must be carefully regulated as to granule size and shape, to minimize resistance to flow of air or other gases passed through it.

Courtesy of the Atlas Powder Company

Activated Carbon Is Especially Important to the Dry Cleaning Industry These Days, Since It Helps Clean Solvents So That They May Be Used Over and Over and Thus Conserve

Carbons intended for food product treatment, or for the purification of chemicals, must be thoroughly washed with acid and water to remove extractable impurities present in the raw material. Unwashed carbons act.vated by heat treatment are invariably alkaline, which is undesirable in many applications, or they may contain compounds of sulfur, iron, aluminum, magnesium, and other common elements. In the chemical industry especially, the introduction of such impurities is often objectionable.

The final step in activated carbon manufacture, after washing, is drying, followed by packing in cartons or bags of suitable weight, and transportation to distributing warehouses or users.

What is the mysterious force exerted by the activated carbon surface, whereby it selects and holds "impurities"? No completely satisfactory explanation is known, but in the case of adsorption from liquids at

least, the following represents a widely held opinion: Those impurities which are susceptible to adsorption on the carbon surface, have the peculiar property of being present in very slightly greater concentration at the air–liquid boundary surface (or interface, as it is called in the language of physical chemistry) than in the body of the liquid.

Courtesy of the Atlas Powder Company

THE HOUSEWIFE MAKES ANOTHER USE OF ACTIVATED CARBON WHEN SHE MAKES PIE AND OTHER PASTRY. COOKING FATS ARE WHITENED AND MADE PURER BY ACTIVATED CARBON.

If a way is provided for removing such an interface, the excess impurity is carried with it, and the concentration of impurity in the liquid is thereby reduced.

This has been demonstrated with soap solutions. The concentration of the "impurity" soap can be reduced in such a solution by beating up a heavy foam, and skimming off the foam. The foam is really a liquid–air interface which is removable. The larger the amount of foam, the larger is the interface area, and the greater is the amount of soap "impurity" drawn from the body of the solution.

It is presumed that impurities also tend to concentrate at a liquid–solid interface, such as that presented by activated carbon dispersed in a liquid. Again, the interface is removable, being held within the sponge-like pore structure of the carbon particle, and goes with the carbon when it is filtered out of the liquid after the treatment has been completed. Again, the greater the area of the carbon–solution interface, the greater the removal of impurity.

The selective character of adsorption (whereby the color and peppermint flavor were removed in our experiment, but the sugar remained unaffected) depends both upon the activating process employed in manufacturing the carbon, and upon the nature of the impurity itself. Materials which are readily soluble, such as sugar in water, or which are simple in their physical and chemical structure, such as metallic salts, are not adsorbed under ordinary circumstances. On the other hand, sparingly soluble substances (such as peppermint oil) and complex substances (such as the red food dye in the candy) are readily adsorbed.

Despite the fact that many theoretical aspects of activated carbon are not yet clearly understood, it is an exceedingly useful tool in the industrial processing of liquids and gases, and appreciation of this fact is constantly leading to new and important uses. Although the man in the street may never during his entire lifetime see or use activated carbon himself, he nevertheless enjoys its usefulness daily in much of the food he eats, the clothes he wears, the home in which he lives, and the automobile which he drives.

OBJECTIVE TESTS IN ORGANIC CHEMISTRY

DURING the past year over 25,000 copies of the coöperative objective tests in organic chemistry were distributed to over one hundred colleges and universities.

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14. Organo-nonmetallic and metallic compounds
15. Alicyclic compounds
16. Benzene, naphthalene, anthracene
17. Aryl halogen compounds
18. Phenols, aryl alcohols, ethers
19. Aldehydes, ketones, quinones
20. Aryl carboxylic acids
21. Aryl sulfonic acids
22. Aryl nitro compounds, amines, and diazonium salts
23. Heterocyclic and miscellaneous compounds
24. Antiseptics, dyes, stains, and indicators
25. Terpenes, rubber, resins, fibers, detergents
26. Processes, reactions, syntheses, and tests
27. Second semester examination, Nos. 10–26

These tests represent an improvement over the 1941–42 series, we believe, with respect to both construction and use. Validity data will be supplied with each set so that out of the twenty items appearing on each test, the instructor may select only a few of the more valid items and thus adapt the test to a five-, ten-, fifteen-, or twenty-minute quiz.

The complete sets are available to instructors of organic chemistry, industrial chemists, or graduate students at a nominal price.

Orders may be placed with the chairman of the committee, Ed. F. Degering, Department of Chemistry, Purdue University, Lafayette, Indiana.

Out of the Editor's Basket

THE American Institute of Physics addressed a letter recently to all state superintendents of education, calling attention to the considerable demand for physicists in the present emergency and urging that everything possible be done to encourage more young people to enter this technical field and to prepare themselves for college training in it. We expect a similar request to proceed very shortly from government circles, applying to other technical fields than physics, especially chemistry and engineering.

● Whatever may have happened to the student attendance in the majority of our colleges and universities, the enrolment in the two-year junior colleges, at least, has increased by 13 per cent in the last year, according to figures recently released by the American Association of Junior Colleges. This increase, despite changed national conditions, is not to be interpreted as a desire of young people to avoid active military service, but on the contrary to their desire to be of the greatest possible service to the country. They are acting on advice by President Roosevelt, Selective Service officials, and college heads, to remain in college until called in order that they may help supply the trained personnel the country so badly needs.

Proof of their patriotic purpose is seen in the decided change in the courses they seek. The special training courses being offered by the junior colleges for direct employment in defense industries are in the front line of popularity with young men, while the young women seem especially interested in the two-year junior college courses for dental and medical assistants and nursing which prepare for the important health fields where there is such a serious shortage of qualified people today.

● The Educational Policies Commission in a pamphlet recently published, entitled "A War Policy for American Schools," states that "without abandoning essential services of the schools, appropriate war duties of the schools should be given absolute and immediate priority in time, attention, personnel, and funds over any and all other activities." The educational "priorities" listed by the Commission are as follows:

Training workers for war industries and services
Producing goods and services needed for the war
Conserving materials by prudent consumption and salvage
Helping to raise funds to finance the war
Increasing effective man power by correcting educational deficiencies
Promoting health and physical efficiency
Protecting school children and property against attack
Protecting the ideals of democracy against war hazards
Teaching the issues, aims, and progress of the war and the peace
Sustaining the morale of children and adults
Maintaining intelligent loyalty to American democracy

In counseling youth with reference to unemployment in the war industries the Commission adds: "There is at present no indication of necessity to reduce the standard total amount or length of public-school education. It is better . . . to adjust academic calendars and class schedules to the war emergency. This can be accomplished by intensifying and accelerating the secondary-school opportunities . . . . Students . . . who are capable of becoming skilled workers should be cautioned against early withdrawal from school to accept 'one-skill' jobs . . . . Youth in trade and industrial schools will ordinarily better serve their country by getting a broad and thorough vocational education which will aid them to move rapidly up the occupational scale to the skilled positions."

In counseling youth with reference to continuing their education "efforts should be made to conserve superior intellectual and other abilities for national service in scientific research and leadership."

● Alpha Chi Sigma, professional chemical fraternity, has initiated this year the development of a Safety Program for its collegiate chapters located in forty-six American colleges and universities.

The objectives of the Safety Program point toward making chemical and chemical engineering students safety conscious in their academic work, give them the proper attitude and training for their later industrial life, and by their example, inculcate among their associates the principles of safety which the Fraternity believes are of utmost value to industry and mankind.

● We congratulate the Detroit section of the American Chemical Society on a venture they have just undertaken. Intensive review courses have been organized for practicing chemists in inorganic, organic, physical, and biological chemistry. This is an effort to keep the chemists of that vicinity up to date and to increase their efficiency. These particular courses consist of 20 lecture hours and run for 10 weeks. No tuition is charged. Perhaps other sections will soon try the same experiment.

● Last month we had something to say about plywood and the plastic airplane question. Those who were interested and would like to follow up the matter further will do well to note the article which *Fortune* carried on this question recently, entitled "Plywood Flies and Fights."

● We learned something interesting about lightning recently. According to information from the Westinghouse Research Laboratories, lightning in the earth's atmosphere brings about combination between nitrogen and oxygen, and then with water, to produce nearly one hundred million tons of nitric acid annually. This is more soil builder than is manufactured by all the world's fertilizer plants.

Lightning also restores the electricity that constantly seeps from the earth to clouds and thus keeps the earth charged. Negative electricity continuously leaks into the skies from the earth at the rate of 1000 amperes. The power represented in this leakage is about 300,000 kilowatts—enough to drive 200 submarines. To offset this loss of electricity, the earth's surface must be struck by lightning at the average rate of 50 times a second, or about two billion times a year. The average stroke carries an electrical charge of 30 coulombs, representing about one billion kilowatts. This is more than the combined output of all the power houses in the world.

● It seems that the progress of "enriched bread" on the market is encountering some resistance. At a recent meeting of the American Association of Cereal Chemists was a discussion of the consumer attitude toward enriched bread. It seems that the opposition comes from several sources—from the whole-wheat zealots, from those who feel that the enriched bread program is nothing but an advertising game, from those who object to the higher price of enriched bread, and from those who are simply ignorant and do not know what is good for them. Proponents point out that the program is only a year old, and was originally designed to be a long-range one. It is also pointed out that while white bread throughout the country is enriched to the extent of about 30 to 35 per cent, those consumers who might be expected to be most intelligent and best informed (such as hospitals and institutions) are recommending the use of enriched flour. There are doubtless both pros and cons in this question, and it will be interesting to see how the movement progresses in the future.

● We have noticed the appearance of an abstract service by Interscience Publishers, Inc., in the general field of Resins–Rubbers–Plastics. We mention this not because we think that this particular technological field will be of particular interest to our readers, but because this sort of thing is really chemical education, and the present example has some rather novel features. The first installment which has come to us is in the form of about 40 pages of loose-leaf abstracts made up in uniform and formalized style which makes reference to them easy.

● Among the many things that have appeared recently on air attacks and incendiary bombs is a little 8-page folder by H. D. Farren entitled "How to Fight Fires Resulting from Air Attacks." It is published by the National Foremen's Institute, Inc., Deep River, Connecticut.

LETTERS

The Carbon Valence Angle

To the Editor:

I have been using for several years in my courses in organic chemistry a method of calculation of the valence angle of carbon, which seems to me simpler than those proposed recently by Gombert[1] and Weatherill.[2] It depends on placing the carbon atom centrally in a circumscribing cube with valence rays emerging through diagonally opposite corners, after the familiar Lewis-Langmuir model (see Figure 1). If the length of a side of the cube be s, and the required valence angle θ, the following relationships are at once apparent:

$$\theta = \text{angle } acb$$

$$\tan \theta/2 = \frac{\overline{db}}{\overline{cd}} = \frac{\frac{1}{2}\sqrt{s^2 + s^2}}{s/2} = \frac{\frac{s\sqrt{2}}{2}}{s/2} = \sqrt{2} = 1.414$$

from which $\theta/2$ is 54° 44′ to a sufficient approximation, and θ is 109° 28′.

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[1] J. CHEM. EDUC., **18**, 336 (1941).

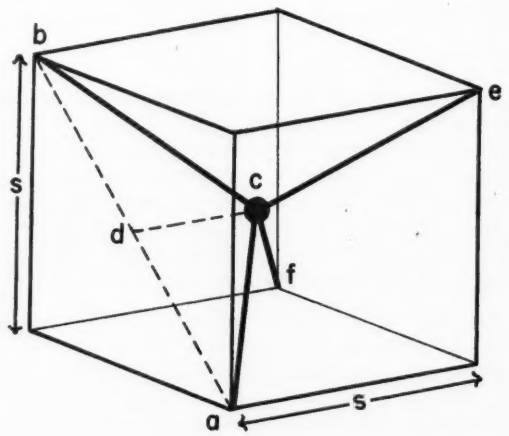

FIGURE 1

c = Central carbon atom; a, b, e, f = Corners traversed by valence rays; d = Center of face diagonal $\overline{ab}$; s = Length of any side; θ = Required angle

[2] J. CHEM. EDUC., **19**, 35 (1942).

RECENT BOOKS

TORCH AND CRUCIBLE. THE LIFE AND DEATH OF ANTOINE LAVOISIER. *Sidney J. French.* Princeton University Press, Princeton, N. J.; Humphrey Milford, London; Oxford University Press, 1941. xi + 285 pp. 15 × 23 cm. $3.50.

This book is different in spirit and in content from the other biographies of Lavoisier which have been published recently. There is no doubt whatever that there is room for it. It describes not merely the scientific work of this man—and describes it critically and lucidly in the light of the most recent historical researches, particularly those of Meldrum—but it also describes the man of affairs, "intimate of some of the greatest figures of the eighteenth century," a "human being caught in a strange mixture of passions and prejudices and swept along by the roaring tide of the French Revolution." The question of Lavoisier's priority and originality is discussed fairly. The matter was, as Berthelot had said, "an incident in the long-standing feud, continually being renewed in the history of science, between the sagacious discoverers of particular facts and the men of genius who frame general theories." The author says (page 179):

"If every accusation charged against Lavoisier were true, it would make no difference. His fame rests not on the originality of his experiments but on the way they were put together. We admire the edifice now for its beauty and utility; we are no longer concerned with the question of who quarried the rock. We admire Lavoisier for the sheer genius he showed, for the tremendous energy he displayed, for the monumental conclusions he obtained, for the magnificent structure he built.

"Both Priestley and Cavendish had the opportunity to do with their own discoveries what Lavoisier did with them. Priestley, in fact, had a better opportunity, for he knew far more about gases than Lavoisier would ever know. Both Priestley and Cavendish were justified in their complaints against Lavoisier's use of their facts. Yet, the world must be thankful that Lavoisier had both the ability and the courage to make use of them."

The book is well documented and well indexed. The only visible illustration is a reproduction of David's painting of M. and Mme. Lavoisier, which, unfortunately, is not included in the book but is printed on the jacket. To a youthful reader, however, with an active imagination, the book will be as full of pictures as a well-remembered movie.

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ORGANIC CHEMISTRY, WITH APPLICATIONS TO PHARMACY AND MEDICINE. *Eldin V. Lynn,* Ph.D., Professor of Chemistry, Massachusetts College of Pharmacy. First Edition. Lea and Febiger, Philadelphia, 1941. 410 pp. 14.5 × 23 cm. $4.50.

The title defines the purpose of the book. The author amplifies his aim by his statement in the preface, "to give an adequate discussion to the important principles of modern organic chemistry and to bring in for purposes of illustration those compounds that are used in pharmaceutical and medical practice." This purpose seems to be ably fulfilled, but the reviewer does not agree with the further statement in the preface that "the text should be equally of value for a course in pharmaceutical organic chemistry where the student has previously studied the general subject." The pharmaceutical and medical applications have been so successfully subordinated to the excellent brief course in organic chemistry itself that the book would almost certainly lose its interest for a student who was already well grounded in the general subject.

This last opinion of the reviewer may seem to be contradicted by the imposing list of pages upon which are found medicinal applications: pages 45, 53, 70, 72, 107, 113, 126, 128, 139, 148–50, 246–9, 252, 259–61, 272–6, 280–3, plus too many pages in the last hundred for listing. The difference in emphasis between this book and the usual general organic chemistry is indicated by this distribution of space. The fact still remains, however, that the pharmaceutical and medical compounds would seem to need considerable amplification in lectures, while the chief value of the book lies in the excellence, combined with the brevity, of its presentation of general organic chemistry.

It is, in fact, remarkable how completely and accurately a subject can be treated in *very* small space, as the following examples show: acetoacetic ester in a single page (219), the tartaric acid isomers also in a single page (137), and the Grignard reagent in only a little over two pages (177–9). In this connection, however, the reviewer suggests that most of the subject matter of Chapter I might easily be omitted, as it is from many organic texts, to afford more room for amplifying the rather too brief treatment of carbohydrates, or, even more important, for including more of the recent theoretical applications in organic chemistry. We note with regret the conservatism of the author with respect to electronic formulas, which he mentions in a single paragraph (page 153) only to discard them, "in order to economize and simplify"; and similarly with respect to resonance, which is not even mentioned in connection with the structure of benzene (page 216).

The treatment of organic nomenclature is excellent throughout, although of course it is less emphasized in the latter half of the book. A very useful list of reference books is included at the end. The Review Questions at the end of each chapter really serve to summarize the chapter and are *very* good for that purpose. As with most organic textbooks, such questions would need to be supplemented by a book on Problems in Organic Chemistry. In the later chapters the Review Questions not only summarize, but supplement the text, thereby aiding in the brevity and conciseness of treatment characteristic of the book. Occasionally also in the text itself the excellent teaching device is used of leaving the reader to produce his own illustrative formulas and equations as, notably, for the problem of orientation on page 219.

The book has the neat orderliness essential to training in organic chemistry; it is almost entirely free from errors and inaccuracies; it is clear and logical; it puts the applications to pharmacy and medicine into their correct relationships to the general subject; and it shows throughout its author's skill and experience as a teacher. It is certainly to be recommended for those for whom it was intended—those who wish a brief concise treatment of the essential facts of organic chemistry, with sufficient mention of the pharmaceutical and medicinal applications to serve as the basis for amplifying lectures.

HELEN S. FRENCH

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A BRIEF COURSE IN ORGANIC CHEMISTRY. A COMBINED TEXTBOOK AND LABORATORY MANUAL. *Reynold C. Fuson,* Professor of Chemistry, University of Illinois, *Ralph Connor,* Associate Professor of Chemistry, University of Pennsylvania, *Charles C. Price,* Assistant Professor of Chemistry, University of Illinois, and *H. R. Snyder,* Assistant Professor of Chemistry, University of Illinois. John Wiley and Sons, Inc., New York City, 1941. x + 248 pp. 24 figs. 15 × 23 cm. $2.50.

This book is designed primarily for the short courses in organic chemistry offered to students of agriculture, home economics, veterinary medicine, pre-dentistry, and pre-medicine. The object is to give the beginner a mastery of the essential principles and important types of organic compounds as soon as possible. Therefore a brief outline of the fundamentals is presented in the first 118 pages, and a more detailed discussion of topics such as recent industrial developments in aliphatic chemistry and the chemistry of various natural products is given in the following 64 pages.

The systematic chemistry is begun with the aliphatic hydrocarbons, and then the aromatic hydrocarbons are described.

The other principal types of compounds follow in the usual sequence. Tables, such as the one showing the relationships between acids and their various derivatives, are excellent teaching aids. The frequent discussion of aliphatic and aromatic types simultaneously is a time-saving arrangement.

The subject matter included is clearly presented and has been, in the main, well chosen. The chapter on amino acids and proteins, however, seems too brief for the students for whom the book is intended; there is no mention of such important amino acids as tyrosine and tryptophane nor of the various classes of simple proteins. In a few theoretical sections brevity may be secured at the expense of clarity.

The chapters on the more advanced topics are very interesting. The survey of recent developments in aliphatic chemistry cannot fail to impress the reader with the extraordinary usefulness and versatility of the hydrocarbons. Such a treatment will probably give the good student a keener appreciation of the possibilities of organic chemistry than if the material were scattered throughout the text. The authors are to be congratulated on the modernity of these chapters. New methods of preparing old intermediates are given, and there is information on such recent products as Lucite, Vinyon, and Nylon, and bacteriocidal agents, such as sulfaguanidine and benzyllauryldimethylammonium chloride (the latter in the section on Coal Tar Products). The chapter on natural products includes an introduction to the essential oils, the terpenes, alkaloids, pigments, vitamins, and hormones.

The twenty-five laboratory experiments, chosen to meet the needs of these groups of students, show a reasonable balance between standard syntheses for teaching organic methods, and test tube experiments to illustrate properties. There are also four experiments for extracting material from natural products, such as lecithin from egg yolk. Of questionable advantage is the inclusion in the laboratory directions of complete equations for the reactions encountered. Some teachers prefer to have such equations given in the descriptive portions of the text, so that students must look them up and hence learn to relate the theoretical and practical work. This disadvantage may be counteracted, however, by the use of the questions after the experiments and proper oral quizzing as suggested by the authors.

Since adequate texts for the classes of students for whom this book is intended are scarce, this book should meet a real need.

ELIZABETH DYER

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PHYSICAL AND CHEMICAL METHODS OF SUGAR ANALYSIS. A PRACTICAL AND DESCRIPTIVE TREATISE FOR USE IN RESEARCH, TECHNICAL, AND CONTROL LABORATORIES. *C. A. Browne*, Ph.D., Formerly Research Chemist of the Louisiana Sugar Experiment Station; Chief of the Sugar Laboratory, U. S. Bureau of Chemistry; Chemist in Charge of the New York Sugar Trade Laboratory; and Chief of the U. S. Bureau of Chemistry, and *F. W. Zerban*, Ph.D., Chemist in Charge of the New York Sugar Trade Laboratory (Formerly Research Chemist of the Louisiana Sugar Experiment Station; Director of the Sugar Experiment Station of Peru; and Research Chemist of the Puerto Rico Sugar Planters' Experiment Station). Third Edition. John Wiley and Sons, Inc., New York City, 1941. xiv + 1353 pp. 332 figs. 15 × 23 cm. $15.00.

The earlier editions have been well recognized as standard valuable handbooks of sugar analysis. The present edition has been entirely rewritten to bring it up to date. It is a comprehensive treatment of all phases of the analysis of sugars, with special reference to cane and beet sugars (sucrose) and the estimation of sugars in foods. It is an invaluable reference book for sugar chemists and food analysts. Chemists who are engaged in general carbohydrate research will find it valuable for reference concerning analytical methods.

C. S. HUDSON

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FUNDAMENTALS OF QUALITATIVE CHEMICAL ANALYSIS. *Roy K. McAlpine*, Ph.D., and *Byron A. Soule*, Sc.D., University of Michigan. Second Edition. D. Van Nostrand Company, Inc., New York City, 1941. xi + 375 pp. 4 figs. 12 tables. 13.5 × 21.5 cm. $2.50.

The second edition of this book follows the same general plan as the first edition and should continue to serve satisfactorily for the second semester course of college chemistry in which qualitative analysis is presented. As in the first edition the first four chapters include review material and a consideration of some important theoretical aspects of qualitative analysis.

Chapter VI treats the lead, silver, mercury (ous) group, Common compounds and reactions are first described and following this the precipitation of the group is discussed. Next are given directions for the precipitation of the group and the separation and identification of the cations. The remainder of the chapter contains a critical review of observations to be used in reporting unknowns, an excellent discussion of the relation of the group to other cation groups, an explanation of the chemistry of the group, and a list of problems and laboratory exercises. The remainder of the cation analysis is treated in a similar manner in chapters VIII to XIII inclusive. Chapter VII is devoted to study aids.

Chapters XIV and XV take up the identification of some common acid radicals. These two chapters leave much to be desired. Chapters XVI and XVII deal with the analysis of dry unknowns.

Chapter IV, which treats the Ionization Theory in Analytical Processes, has been rewritten and expanded. Chapter V, in which the student is introduced to laboratory technic, has been expanded to include several pages of description of semimicro technic.

The second edition of this book should continue to serve both instructor and student well. It must be considered a valuable addition to the chemical literature.

LYMAN J. WOOD

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FUNDAMENTALS OF CHEMISTRY. *L. Jean Bogert*, Ph.D., formerly Instructor in the Department of Medicine, University of Chicago; Instructor in Experimental Medicine, Yale Medical School, and Lecturer in Chemistry, Connecticut Training School for Nurses, New Haven; Professor of Food Economics and Nutrition, Kansas State Agricultural College, Manhattan; Research Chemist, Obstetrical Department, Henry Ford Hospital, Detroit. Fifth Edition, Revised. W. B. Saunders Company, Philadelphia and London, 1941. xix + 528 pp. 74 figs. 13.5 × 19.5 cm. $3.00.

In recognition of the demand by schools of home economics and nursing for a textbook which covers the fundamentals of inorganic, organic, and physiological chemistry on an elementary level, this well-known textbook has been expanded in the fifth edition by the addition of several new chapters on organic chemistry and its applications to physiology. The chapter on vitamins has been rewritten and throughout the book extensive revisions have been made in line with recent developments. The treatment is primarily factual. No attempt is made to incorporate more than a smattering of atomic structure, and radioactivity is covered in two pages. The Arrhenius theory of electrolytic solutions only is mentioned and none of the basic concepts of chemistry are developed systematically. The sections devoted to purely descriptive chemistry are remarkably free from misleading statements. The textbook is successful in the hands of students who have studied chemistry in secondary schools and may be recommended as a text for short courses in applied chemistry where factual knowledge of the subject is stressed, rather than training in the use of the scientific method. The booklet of Study Plans, issued with previous editions, is not available for the present volume.

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